









AMERICAN SCIENCE SERIES, BRIEFER COURSE

AN INTRODUCTION TO THE STUDY

OF

CHEMISTRY

BY

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TO MARY  
ANNABELLE

## PREFACE.

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IN preparing this book, I have endeavored to keep in mind the fact that it is intended for those who are beginning the study of chemistry. Instead of presenting a large number of facts and thus overburdening the student's mind, I have presented a smaller number than is usual in elementary courses in chemistry; but I have been careful to select for treatment such substances and such phenomena as seem to me best suited to give an insight into the nature of chemical action. Usually the mind is not allowed to dwell for any length of time upon any one thing and thus to become really acquainted with it, but is hurried on and is soon bewildered in the effort to comprehend what is presented. I cannot but believe that it is much better to dwell longer on a few subjects, provided these subjects are properly selected.

The charge is frequently made that our elementary textbooks on chemistry are not *scientific*; that is to say, that not enough stress is laid upon the relations which exist between the phenomena considered,—the treatment is not systematic. The student is taught a little about oxygen, a little about hydrogen, a little about nitrogen, etc.; and then a little about potassium, a little about calcium, etc.; and he is left simply to wonder whether there is any connection between the numerous facts offered for study. It must be acknowledged that there are serious difficulties in the way of a purely scientific treatment of chemistry, but I think

that it is quite possible to treat the subject more scientifically than is customary, and thus to make it easier of comprehension to the student. I have made an effort in this direction in the book here offered to the public.

In teaching chemistry, two mistakes are commonly made. The first is that of presenting the profoundest theories of the science before the student is prepared for them. Hence they make little impression upon his mind, and he only learns to repeat words about them, without having any real comprehension of them.

The other mistake is that of giving directions for experiments without making it clear to the student why they are performed or what they teach. The result is that he sees little or no connection between the subjects treated in the text-book and the things which he works with in the laboratory.

Now, the first object of a course in science should be to develop a scientific habit of thought. This cannot be done by mere study of the theories of a science, nor by haphazard experimenting. It can only be reached by systematic study of the phenomena, and by recognizing the connection between these phenomena and the theories. At the outset the best plan is to study phenomena scientifically, and afterwards speculations may be introduced to some extent; though, in my opinion, it is better to keep these decidedly subordinate in an elementary course.

> At this day it is almost superfluous to emphasize the great importance of laboratory work as a part of a course in chemistry. College authorities and school boards are beginning to recognize the necessity of this kind of work for the purpose of securing satisfactory results. A laboratory can be fitted up at slight cost in which all the experi-

ments described in this book could be performed. It is not necessary to wait until a complete laboratory is provided. The accommodations needed are simple, and there can hardly be a college or school which could not with a little effort secure the few conveniences. Should there, however, be such a place, the teacher can at least perform the experiments described. And this he had better do with not more than ten or a dozen students around him. By constantly questioning them, and getting one or another to help him, or to do the work, fairly satisfactory results can be attained.

>If the students work in the laboratory, it is of prime importance that they should not be left to shift for themselves. They will surely acquire bad habits of work, and will generally fail to understand what they are doing. A thorough system of questioning and cross-questioning is necessary in order that the work shall be successful. A badly constructed piece of apparatus should not be allowed, and cleanliness should be insisted upon from the beginning. The instructor should be as watchful in the laboratory as in the recitation-room, and should be as exacting in regard to the experimental work as the teacher of languages is in regard to the words of a lesson. A badly performed experiment should be considered as objectionable as a bad recitation or a badly written exercise. When teachers of chemistry acquire this feeling, and work in this spirit, the educational value of laboratory courses will be greater than it frequently is now. The average playing with test-tubes and precipitates is of questionable benefit. As it has been dignified by the undeserved name of scientific training, and put forward in place of the real thing, many thinking men have been led to question the value of scientific training,

and to adhere to the old drill in grammatical forms and mathematical problems. I do not wonder at this, but I should be greatly surprised to find this state of mind continuing after really good laboratory courses are provided. A slovenly laboratory course in chemistry is a poor substitute for a well-conducted course in mathematics or languages. It behooves those who are convinced of the great advantages to be derived from good laboratory courses to see to it that these courses are conscientiously conducted.

A few of the experiments described in the book cannot well be made by every student in the laboratory. These the teacher should make at all events, and he should not only make them, but see to it that every detail is thoroughly comprehended by the student. In the directions for the experiments the quantities recommended are in some cases larger than would be desirable for each student. The proportions being correctly given in the book, the absolute quantities can be regulated by the teacher to suit the circumstances.

Finally, I invite correspondence from teachers who may use the book, and who may experience any difficulty in its use. I shall gladly avail myself of any suggestion which may help towards making it more useful.

The apparatus needed can be obtained from any dealer in chemical wares, and I have no doubt that some of the larger houses would furnish estimates for all that is necessary for the purpose of illustrating the course.

I. R.

BALTIMORE, December 21, 1885.

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# AN INTRODUCTION TO THE STUDY OF CHEMISTRY.

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## CHAPTER I.

### CHEMICAL ACTION.—ELEMENTS.—COMPOUNDS.—HOW TO STUDY CHEMISTRY.

THOSE things which are most familiar to us are apt to be regarded with least wonder and to occasion the least thought. It is only when we come to study them with care that we begin to see how wonderful they are; and if we study them in the proper way, the more we study them the more interesting do they become. We are all familiar with a great many changes which are taking place in the things around us, but unless we have studied some of the natural sciences these changes make only a superficial impression on us, or if they awaken thought at all, that thought is necessarily indefinite and unsatisfactory. Take, for example, the changes included under the head of fire. Unless we have studied these changes with care, what can we make of them? We see substances destroyed by fire. They apparently disappear. We feel the heat produced by the burning. We know that this heat disappears, and we have nothing left in the place of the substance which burned. We know that some things will burn and others will not. This is about all we know unless we have studied Chemistry, which has to deal with all such changes as

those produced by fire. Take, as another example, the rusting of iron. We all know that iron when exposed to the air undergoes a serious change, becoming covered with a reddish-brown substance which we call rust. If the piece of iron is comparatively thin, and it be allowed to lie in the air long enough, it will be completely changed to the reddish-brown substance, and no iron as such will be left. If the juices from fruits, as from apples, be allowed to stand in contact with air they undergo change, becoming sour, and a somewhat similar change takes place in milk. If we bring a spark in contact with gunpowder there is a flash and the powder disappears, dense smoke appearing in its place. Think for a moment. What are the causes of these remarkable changes? Can we learn anything about them by study? If we can, surely the study is worth undertaking.

In those changes which have been referred to, the substances changed disappeared as such. After the fire the wood or the coal, or whatever may have been burned, was no longer to be found. The rusted iron is no longer iron. The gunpowder after the flash is no longer gunpowder. Changes of this kind in which the substances disappear and something else is formed in their place are known as chemical changes, and CHEMISTRY is the science which has to deal with changes in the composition of substances.

There are many changes taking place which do not affect the composition of substances. Iron, for example, may be changed in many ways and still remain iron. It may become hotter or colder. There is certainly a difference between a hot piece of iron and a cold piece. Its position may be changed, or, as we say, it may be moved. The difference between a piece of iron moving and a piece

at rest is a very wonderful one, though we are not, as a rule, much impressed by the difference. The iron may be struck in such a way as to give forth a sound. While giving forth the sound its condition is certainly different from that in which it does not give forth sound. The iron may be made so hot that it gives light. When, for example, it becomes "red-hot" we can see it in a dark room. It may further be made so hot that it gives off a great deal of light, as when it is "white-hot." A piece of iron may be changed further by connecting it with what is known as a galvanic battery. A current of electricity then passes through it, and we can easily recognize the difference between a piece of iron through which a current of electricity is passing and one through which no current is passing. The former when brought into certain liquids will at once change their composition, while the latter will produce no change. Finally, when a piece of iron is brought in contact with a piece of loadstone, it acquires new properties. It now has the power to attract and hold to itself other pieces of iron. In all these cases, then, the iron is changed, but it remains iron. After the moving iron comes to rest it is exactly the same thing that it was before. After the iron which is giving forth sound has ceased to give forth sound, it returns to its original condition. Let the heated iron alone and it cools down, ceasing soon to give off light, and giving no evidence of being warm. Remove the iron from contact with the galvanic battery and it loses those properties which are due to the current of electricity. In time, the iron which is magnetized by contact with the loadstone loses its magnetic properties. It no longer has the power to attract other pieces of iron. It does not differ from ordinary iron. But, as we have seen, if iron has been changed by rust-

ing it is no longer iron. It is another substance, and, no matter how long the rust may be allowed to lie unmolested, it will not return to the form of iron. Iron may, further, be changed by contact with other substances than air so as to lose its properties. Strong vinegar, which contains the substance known to chemists as acetic acid, acts upon iron, causing it to lose its properties. A new substance is formed. The substances known as muriatic or hydrochloric acid, nitric acid, and sulphuric acid also act upon iron and give rise to the formation of new substances which have not the properties of iron.

From what has been said in regard to the kinds of change which iron can undergo, we see that these changes are of two kinds:

1st. Those which do not permanently affect the iron.

2d. Those which do permanently affect the iron and which necessarily cause the formation of new substances with properties quite different from those which belong to the iron. What is true of iron is true in general of all other substances. We therefore have two classes of changes presented to us for study:

1st. Those which do not affect the composition of substances.

2d. Those which affect the composition of substances and give rise to the formation of new substances with new properties.

Changes of the first kind are called *physical changes*. Those of the second kind are called *chemical changes*.

That branch of knowledge which has to deal with physical changes is known as PHYSICS. And that which has to deal with chemical changes is known as CHEMISTRY.

Everything that has to do with motion, with heat, light,

sound, electricity, and magnetism, is studied under the head of Physics. Everything that has to do with the composition of substances and changes in the composition is studied under the head of Chemistry.

Although at first sight these different kinds of change appear to be quite distinct from one another, they are, in reality, closely related. If a body in motion be stopped suddenly, it becomes hot. Many examples of a similar transformation of motion into heat are familiar: A wire becomes hot when hammered on an anvil; a coin rubbed on cloth becomes hot. In both cases the cause of the heat is the interference with the motion. The hammer is stopped and becomes hot; the coin is not stopped, but the motion is interfered with, and we have to push harder in order to move it over the cloth than we would to move it in the air. A wire through which a current of electricity is passing is heated, and if the wire is small and the current strong it will become so hot that it will give off light. Here the electricity causes heat and light. Again, we know that by means of heat we can produce motion. The steam-engine is the best example of this kind of transformation. We build a fire; this heats the water in the boiler; the water is converted into steam, which expands and moves the piston, and the motion of the piston is the seat of all the complex motions which are found in the different parts of the engine. The train or the ship moves. What moves it? Plainly, the heat is the cause of the motion. But we can go a step farther back and ask what causes the heat? The answer is obvious. It is the burning of the fuel. But, in burning, the composition of the fuel is completely changed. A change is produced which in itself is not heat. When a piece of coal burns, then, it is

undergoing a change in composition, and, as a result of this change, heat is produced. The heat is, therefore, produced by a chemical change in the coal, and we may say that the motion of the steam-engine is the result of the chemical change taking place in the coal or wood which, in burning, produces the heat.

Just as in all ordinary fires we have heat produced as a result of chemical changes in the fuel, so we may have chemical changes produced by heat or by electricity.

**EXPERIMENT 1.**—In a clean, *dry* test-tube put enough white sugar to make a layer  $\frac{1}{4}$  to  $\frac{1}{2}$  an inch thick. Hold

the tube in the flame of a spirit-lamp or a laboratory burner, as shown in Fig. 1.

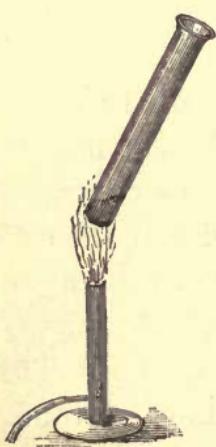


FIG. 1.

Liquids are given off and these condense in the upper part of the tube. A black mass, charcoal, remains behind. It is evident that a change in composition has been effected. There is no sugar left. In place of the familiar, white, sweet substance which dissolves in water, we have left a black, tasteless substance

which does not dissolve in water. This change has been produced by heat.

**EXPERIMENT 2.**—From a piece of glass tubing of about 6 to 7 millimetres ( $\frac{1}{4}$  inch) internal diameter cut off a piece about 10 centimetres (4 inches) long by making a mark across it with a triangular file, and then seizing it with both hands, one on each side of the mark, pulling and at the same time pressing slightly as if to break it. Clean and dry it, and hold one end in the flame of a laboratory burner until it melts together. During the melting

turn the tube constantly around its long axis so that the heat may act uniformly upon it. Put into it enough red oxide of mercury (mercuric oxide) to form a layer about 12 millimetres ( $\frac{1}{2}$  inch) thick. Heat the tube as in the last experiment. You will notice that the color of the substance is changed, and after a time minute globules of mercury will be deposited in the upper part of the tube, and, on cooling, these will collect together and fall down, so that the presence of the mercury is readily seen. If during the heating a splinter of wood which has a spark on the end be thrust into the tube, the spark will burst into flame and the wood will burn much more actively than it would in the air. By taking it out of the tube and putting it back again a few times, the difference between the burning in the tube and out of it will be shown very clearly. We see thus that by heat the red oxide of mercury is changed. We get in place of it mercury, which we see in the tube, and an invisible substance which is evidently in the tube, as is shown by the active burning of the wood. The red oxide of mercury has disappeared, and new substances have appeared in its place. A change in composition has been effected. Or a chemical change has been caused by heat.

In a galvanic battery there are always substances which are undergoing changes in composition, and the electric current is due to these changes. It is therefore true that electric currents are produced by chemical changes. A simple form of a battery is represented in Fig. 2.

The plates marked *k* are of copper, those marked *z* of zinc. The plates are connected together by wires, as shown. In each vessel there is poured a mixture of sulphuric acid and water. This mixture acts upon the zinc, producing a

chemical change in it. This is the cause of the electric current which passes through the wire. As has already been stated, this wire not only conducts the electric current,

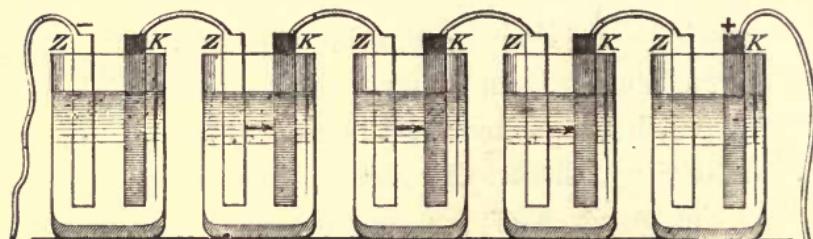


FIG. 2.

but also becomes heated. Here, then, we have an electric current caused by chemical change, and heat caused by the electric current.

As has been said, an electric current has the power to cause changes in composition, or chemical changes. This may be well illustrated by the action of a current on water.

**EXPERIMENT 3.**—To the ends of the copper wires connected with two cells of a Bunsen's or Grove's battery fasten small platinum plates say 25 mm. (1 inch) long by 12 mm. ( $\frac{1}{2}$  inch) wide. Insert these platinum electrodes into water contained in a small shallow glass vessel about 15 cm. (6 inches) wide and 7 to 8 cm. (3 inches) deep, taking care to keep them separated from each other. No action will take place, for the reason, as has been shown, that water will not conduct the current, and hence when the platinum electrodes are kept apart there really is no current. By adding to the water about one tenth its own volume of strong sulphuric acid, it acquires the power to convey the current. It will then be observed that bubbles rise from each of the platinum plates. In order to collect them we may arrange an apparatus as shown in figure 3.

*A* and *B* represent glass tubes which may conveniently be about 30 cm. (1 foot) long and 25 mm. (1 inch) internal diameter. They are first filled with the water containing one tenth its volume of sulphuric acid, and then placed with the mouth under water in the vessel *C*. The platinum electrodes are now brought beneath the inverted tubes. The bubbles which rise from them will pass upward in the tubes and the water will be pressed down. Gradually the water will be completely forced out of one of

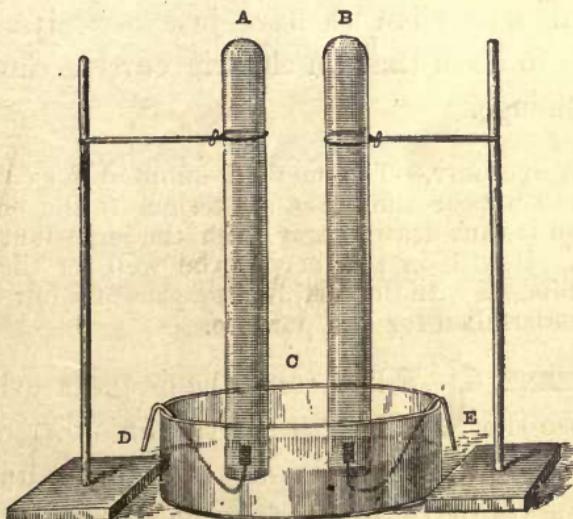


FIG. 3.

the tubes, while the other is still half full of water. The substance which we have thus collected in each of the tubes is an invisible gas. After the first tube is full of gas, remove it by placing the thumb over the mouth. Turn it mouth upward and at once apply a lighted match to it. A flame will be noticed. The gas which was contained in the tube is therefore capable of burning. It cannot, therefore, have been air. In the mean time the second tube will have become filled with gas. Remove this tube in the same way and insert a thin piece of wood with a spark on it. The spark

will at once burst into flame, and the burning of the wood will take place more actively than it does in ordinary air, as may be shown by withdrawing it and again inserting it into the tube. The gas in this tube, it will be noticed, does not take fire. Without going into further details, it is clear from the above experiment that when an electric current acts on water two invisible gases are produced. We shall have occasion hereafter to study this experiment much more carefully, and we shall find that from it we can learn a great deal more than we have just learned; but our object now is to learn that an electric current can produce a chemical change.

**NOTE FOR STUDENT.**—The method adopted for collecting the gases is apt to appear somewhat mysterious to the beginner, and his attention is thus drawn away from the important part of the experiment. It will on this account be well for the student to familiarize himself with the method by means of a few experiments especially undertaken for the purpose.

**EXPERIMENT 4.**—Fill a test-tube or glass cylinder with water ; close the mouth with the thumb or a ground-glass plate ; invert the tube, and put the mouth under water. The water stays in the tube after the thumb or glass plate is removed. (Why ?) Now take a piece of glass or rubber tubing ; put one end under the mouth of the inverted tube, and blow gently through the other end. Bubbles will rise in the tube and the water will be displaced. In this case the gases from the lungs are collected. When they come below the mouth of the tube, being lighter than water, they rise, and as the space occupied by them cannot be occupied by the water too, the latter is displaced. (See Fig. 4.)

**EXPERIMENT 5.**—To transfer a gas from one vessel to another by displacement of water, place both vessels inverted in the same bath, and then gradually bring the one con-

taining the gas mouth upward, below the one containing the water. (See Fig. 5.)

The above examples will suffice to prove that the differ-

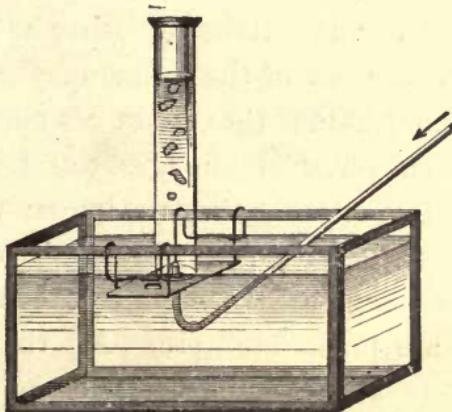


FIG. 4.

ent kinds of changes, both physical and chemical, are more closely related to one another than they appear to be at first sight. In consequence of this relation, we cannot deal with chemical changes without constantly having to

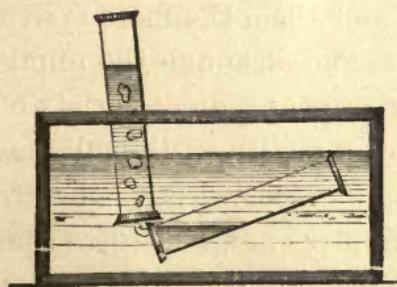


FIG. 5.

deal with physical changes. For a thorough understanding of chemical changes it is necessary to have some knowledge of the changes produced by heat and electricity. We

shall find that whenever chemical changes take place, heat changes and electric changes also take place. And we shall find, too, that, in order to bring about chemical changes, we frequently make use of heat and electricity. If, therefore, the student has not studied physics, he should familiarize himself with a few of the elementary facts of the science before undertaking the study of chemistry.\* He should know what physical changes can be produced by heat; what boiling is; what evaporation is; what condensing a vapor means; what the expression "to pass an electric current" means; how the more common forms of galvanic batteries are made, etc., etc. All these matters are of importance in studying chemical changes, and still a text-book of chemistry is not the proper place to treat them. It will therefore be assumed that the student has this knowledge.

Everything that has to do with the composition of substances is the object of the chemist's study. It is plain to every one that the number of substances of different kinds found in nature is very great, and the study of their composition appears to be an almost hopeless task; but the more we learn about them the more systematic our knowledge will become, and although the number of substances is large and they present a great variety of properties, still the subject is not in reality so difficult as it seems. Most of the substances we meet with can by proper methods be separated into simpler ones, and these again into still simpler ones which cannot be further decomposed by any means known to us. Such substances as cannot be decom-

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\* A simple book which treats of the essential elementary facts of physics is Balfour Stewart's "Primer of Physics." It is well worth a careful study.

posed into simpler ones by us are called elements. Now, although there are thousands and thousands of different kinds of substances met with in nature, these are really made up of a comparatively small number of simple substances or elements. The number of elements thus far discovered is between sixty and seventy, but the larger number of these are rare, and we might have a very excellent knowledge of the essentials of chemistry without any knowledge of these rare elements. We shall find that most things we have to deal with are really made up of about a dozen elements, and that most of the chemical changes which are taking place around us, and which we need to study in order to get an insight into the nature of chemical action, take place between this small number of elements. In studying the principles of astronomy it is not necessary to consider every known heavenly body; and in studying the essentials of zoology it is not necessary to study every known animal. So, also, in studying the essentials of chemistry it is not necessary to study all known substances. We should rather endeavor at first to select such substances and such examples of their action upon one another as are of fundamental importance, and study these with some care. By so doing we shall get a really better knowledge of chemical substances and chemical changes than we should by studying more superficially a larger number of substances and changes.

**Mechanical Mixtures and Chemical Compounds.**—Most of the substances found in nature are made up of several others. Wood, for example, is very complex, containing a large number of distinct substances intimately mixed together. Some of these can be isolated, but it is impossible to isolate them all with the means at present at our com-

mand. Most of the rocks met with are also quite complex, and it is a difficult matter to isolate the constituents. If we look at a piece of coarse-grained granite we see plainly enough that it contains different things mixed together, and if it be broken up we can pick out pieces of different substances from the mass. If we now examine a piece of each of the different substances thus picked out of the granite, it appears to be homogeneous, *i.e.*, we cannot recognize the presence of more than one kind of thing in any one piece. If the piece is carefully selected it may be powdered finely in an agate mortar, and some of the powder examined with a microscope without the presence of more than one substance being recognized. We are able to isolate three substances from granite by simply breaking it up and picking out pieces of different kinds. We might therefore conclude that granite consists of three substances. This is true, but it is not the whole truth. For it is possible by proper means to get simpler substances from each of the three already separated. This, however, is a much more difficult process than the separation first accomplished. To effect the separation of each of the three constituents of granite into its elements requires more powerful means. Substances must be brought in contact with them which act upon them, changing their composition, *i. e.*, act chemically upon them, and high heat must be used to aid the action. By hard and skilful work it is possible to separate the three components of granite into their elements.

**EXPERIMENT 6.**—The teacher should provide a piece of coarse-grained granite, and ask the students to separate the three components and to note the differences between them. One of the pieces should then be pulverized and some of the powder put on the slide of a microscope, and each student asked to examine the powder.

From the above observations and statements we see that substances may be united in different ways. They may be so united that it is a simple thing to separate them by mechanical processes. Or they may be so united that it is impossible to separate them by mechanical processes. By a mechanical process is meant any process which does not involve the use of heat, electricity, or chemical change. Thus, the mechanical process made use of in the case of granite consisted in picking out the pieces. The separation of particles of different sizes by means of a sieve is a mechanical process. The separation of two liquids which do not mix with each other is a mechanical process. If we rub together in a mortar a little sulphur and iron filings, it makes no difference how intimately we may mix them, they remain iron and sulphur. The mixture may appear to the naked eye to be homogeneous, but the microscope will show the particles of iron lying side by side with the particles of sulphur.

**EXPERIMENT 7.**—Mix a gram or two of powdered roll-sulphur and an equal weight of very fine iron filings in a small mortar. Examine a little of the mixture with a microscope.

Not only can we recognize the particles of iron and of sulphur by means of the microscope, but we can also pick out the pieces of iron by means of a magnet. The magnet attracts the iron but not the sulphur, so that by passing the magnet often enough through the mixture we can pick out all the iron and leave all the sulphur. This separation is really a mechanical separation. It is only a somewhat more refined method of picking out than that used in the case of granite.

**EXPERIMENT 8.**—Pass a small magnet through the mix-

ture above prepared. Unless the substances used are thoroughly dry, particles of sulphur will adhere to the magnet, but even then it will be seen that most of that which is taken out of the mixture is iron.

The iron and sulphur may also be separated by treating the mixture with a liquid known as bisulphide of carbon. Sulphur dissolves in this liquid, but iron does not. So that when the mixture is treated with it the iron is left behind, and can easily be recognized as such.

**EXPERIMENT 9.**—Pour two or three cubic centimetres of bisulphide of carbon on a little powdered roll-sulphur in a dry test-tube. The sulphur dissolves. Treat iron filings in the same way. The iron does not dissolve. Now treat a small quantity of the mixture with bisulphide of carbon. After the sulphur is dissolved pour off the solution on a good-sized watch glass and let it stand. Examine what remains undissolved in the test-tube and satisfy yourself that it is iron. After the liquid has evaporated examine what is left in the watch glass and satisfy yourself that it is sulphur. Why are you justified in concluding that the substance left in the test-tube is iron and that left on the watch glass is sulphur?

The mixture of iron and sulphur with which we have been experimenting is a mechanical mixture. It contains iron and sulphur as such. The iron is attracted by the magnet, just as if the sulphur were not present. The sulphur burns, just as if the iron were not present. The sulphur further dissolves in bisulphide of carbon, just as if the iron were not present. The mixture possesses the properties of both of its constituents.

We may allow the mixture of sulphur and iron to lie for any length of time, and it will remain simply a mechanical

mixture. If, however, we put it in a test-tube and heat it, a remarkable change takes place. At first the sulphur melts and becomes dark-colored. It may even take fire. But soon something else evidently takes place. The whole mass begins to glow, and if we at once take the tube out of the flame, the mass continues to glow, becoming brighter. This soon stops; the mass grows dark and gradually cools down. As soon as it reaches the ordinary temperature, the tube should be broken and the contents put in a mortar. A close examination will show that the mass does not look like the mixture of sulphur and iron with which we started. It has a bluish-black color and is apparently homogeneous. An examination with the microscope, the magnet and bisulphide of carbon will prove that, while there may be a little iron left, and possibly a little sulphur, most of the bluish-black mass is neither iron nor sulphur, but a new substance with properties quite different from those of iron and from those of sulphur.

**EXPERIMENT 10.**—For the purpose of the experiments just described make a fresh mixture of three grams each of powdered roll-sulphur and fine iron filings. Grind them together very intimately in a dry mortar and put them in a dry test-tube. Heat until the mass begins to glow.

The new substance formed as the result of the action of the sulphur and iron upon each other is no longer a mechanical mixture. We cannot decompose it by a mechanical process. The constituents are much more firmly united than they were in the mixture. They have lost their identity. They are both present, to be sure, but by means of any ordinary examination we cannot recognize them, as their properties have been lost. When the mixture began to glow, the act of combination began, and the glowing

was a result of the act of combination. The sulphur and iron combined with each other chemically, and formed a chemical compound. They did not act upon each other when simply brought in contact. It was necessary to heat the mixture in order to cause chemical combination to take place. The heat in this case helped the chemical action. But after the action began it continued without further aid and produced heat, as was shown by the glowing of the mass.

The essential feature of the action in the case of iron and sulphur, just discussed, is this: that the substances which act upon each other lose their own properties and something is formed with entirely new properties. This is true of every case of chemical action, and it is one of the chief characteristics of that kind of action. If we should examine a number of cases of chemical action, we might be inclined to think that they had no common features; but this loss of properties and the formation of new substances always take place. A few examples will help to show the truth of this statement.

**EXPERIMENT 11.**—Examine a piece of calc-spar or marble. You see that it is made up of pieces of definite shape. It is, as we say, crystallized. It is quite hard, though a knife will cut it. Heated in a small glass tube, as in Experiment 2, it does not melt, but remains essentially unchanged. It does not dissolve in water. To prove this, put a piece the size of a pea in a test-tube with pure water. Thoroughly shake, and then, as heating usually aids solution, boil. Now pour off a few drops of the liquid on a piece of platinum\* foil or a watch glass, and by gently heat-

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\* Platinum, an expensive metal, finds extensive use in chemical laboratories, for the reason that it resists the action of heat and of most chemical substances.

ing cause the water to evaporate. If there is anything solid in solution there will be a residue on the platinum foil or watch glass. If not, there will be no residue. Now treat a small piece of the substance with dilute hydrochloric acid and notice what takes place. Bubbles of gas are given off. After the action has continued for about a minute, insert a lighted match in the upper part of the tube. It is extinguished and the gas does not burn. The gas formed in this case is therefore plainly not identical with either one of those obtained from water by the action of the electric current (see Experiment 3). It is what is commonly called carbonic acid gas. As the action continues the piece of calc-spar or marble grows smaller and smaller and finally disappears, when we have a clear solution. The substance has dissolved in the hydrochloric acid. In order to determine whether anything else has taken place besides the dissolving, we shall have to get rid of the excess of hydrochloric acid. This we can easily do by boiling it, when it passes off in the form of vapor, and then whatever is in solution will remain behind. For this purpose put the solution in a small, clean porcelain evaporating-dish, and put this on a vessel containing boiling water, or a water-bath. The operation should be carried on in a place in which the draught is good, so that the vapors will not collect in the working-room. They are not poisonous, but they are annoying. The arrangement for evaporating is represented in Fig. 6.

After the liquid has evaporated and the substance in the evaporating-dish is dry, examine it and carefully compare its properties with those of the substance which was put into the test-tube. Its structure will be found not to present the regularities noticed in the original substance. It is much softer. It dissolves in water. It melts when heated

in a tube. It does not give off a gas when treated with hydrochloric acid. When exposed to the air it soon becomes moist, and after a time liquid. The experiment shows us that when hydrochloric acid acts upon calc-spar or marble,



FIG. 6.

the latter at least loses its own properties. It might be shown that some of the hydrochloric acid also loses its properties. In place of the two we get a new substance with entirely different properties. The two substances have acted chemically upon each other and produced a chemical compound. In this case it was only necessary to bring the

substances in contact in order to cause them to act chemically upon each other. It was not necessary to heat them, as it was in the case of the iron and sulphur.

**EXPERIMENT 12.**—Bring together in a test-tube a small piece of copper and some moderately dilute nitric acid. In a short time action begins. The upper part of the tube becomes filled with a dark, reddish-brown colored gas which has a disagreeable smell. Do not inhale it, as when taken into the lungs it produces bad effects. The solution becomes colored dark blue, and the copper disappears. Examine this solution, as in Experiment 9, and see what has been formed. What are the properties of the substance found after evaporation of the liquid? Is it colored? Is it soluble in water? Does it change when heated in a tube? Is it hard or soft? Does it in any way suggest the copper with which we started?

**EXPERIMENT 13.**—Try the action of dilute sulphuric acid on a little zinc in a test-tube. A gas will be given off. Apply a lighted match to it. Does the result suggest anything noticed in an experiment already performed? After the zinc has disappeared evaporate the solution as in Experiments 9 and 10. Carefully compare the properties of the substance left behind with those of zinc.

**EXPERIMENT 14.**—Hold the end of a piece of magnesium ribbon about 20 centimetres (8 inches) long in a flame until it takes fire; then hold the burning substance quietly over a piece of dark paper, so that the light white product may be collected. Compare the properties of this white product with those of the magnesium. Here again a chemical act has taken place. The magnesium has combined with something which it found in the air, and heat was produced by the combination. The product is the white substance.

**EXPERIMENT 15.**—In a small, dry flask (400 to 500 ccm.) put a bit of granulated tin. Pour upon it 2 or 3 ccm. concentrated nitric acid. If no change takes place, heat gently and presently there will be a copious evolution of a reddish-brown gas with a disagreeable smell, (under what conditions has a gas like this already been obtained?) the tin will disappear, and in its place will appear a white powder. Compare the properties of this white powder with those of tin. Why are you justified in concluding that they are not the same thing?

Experiments like those just performed might be multiplied indefinitely. But a sufficient number have already been studied to show upon what kinds of observations is based the statement that:

*Whenever two or more substances act upon one another*

*chemically they lose their own properties, and new substances are formed with entirely different properties.*

**Relative Quantities of Chemical Elements which Act upon one Another.**—A magnet of a certain strength will support a piece of iron of a certain weight. But it will also support any piece of iron weighing less. It shows no preference for certain weights of iron. So, also, the earth attracts all bodies, light or heavy, showing no preference for certain weights. When substances act upon one another chemically, however, it is found that a certain weight of one will combine with a definite weight of another, and only with this weight—no more and no less. Take again, for example, the case of iron and sulphur. If equal weights of these elements be mixed and caused to act chemically by the aid of heat, it will be found that some of the sulphur is left over in the uncombined state after the action is over. If we should take twice as much iron as sulphur, then, after the action, some iron would be left over. If we were to make a large number of experiments with great care, we should find that when the two elements are mixed in the proportion of seven parts of iron to four parts of sulphur the action is perfect, neither iron nor sulphur being left over. If we study other cases of chemical action in the same way, we find that each element exhibits a tendency to unite with others in quantities which can always be expressed by the same figure. Let us return to the examples already studied. See Experiments 10, 14, 15. When magnesium burns it really combines with oxygen, as will be shown later. The quantities of magnesium and oxygen which combine bear to each other the relation 3:2. We can, of course, express this fact by saying that the compound of magnesium and oxygen contains,—

Magnesium, 60 per cent,  
and Oxygen, 40 " "

When nitric acid acts upon tin it gives up oxygen, and the white substance formed is a compound of tin and oxygen. If this is perfectly dried it is found to contain tin and oxygen in the proportion of 59 parts of tin to 16 parts of oxygen, or its composition is,—

Tin, 78 $\frac{2}{3}$  per cent;  
Oxygen, 21 $\frac{1}{3}$  " "

The oxide of mercury, which was used in Experiment 2, contains mercury and oxygen in the proportion of 25 parts of mercury to 2 parts of oxygen, or its composition is,—

Mercury, 92.59 per cent;  
Oxygen, 7.41 " "

The elements, sulphur and oxygen, unite under certain circumstances and form a compound containing an equal weight of each, or its composition is,—

Sulphur, 50 per cent;  
Oxygen, 50 " "

An extensive examination has shown conclusively that each chemical compound always contains the same elements in exactly the same proportions. The compound of sulphur and iron always contains exactly 36.36 per cent of sulphur and 63.64 per cent of iron. The compound of magnesium and oxygen always contains exactly 60 per cent of magnesium and 40 per cent of oxygen, and so on throughout the list of chemical elements. These facts were discovered by the united efforts of a large number of chemists continued through several years. They are of very great

importance. They are summed up in the general statement.

*Chemical combination always takes place between definite masses of substances.*

This is known as the *law of definite proportions*. It is simply a statement of what we have every reason to believe to be the truth. Every fact known to us in regard to chemical combination is in accordance with this general statement. It expresses what we learn by a study of chemical facts. It must be borne in mind that this law, as well other laws governing natural phenomena, can never be proved to be absolutely true, for the reason that we cannot examine every case to which the law applies. But if, after examining a very large number of cases, we find that the law always holds true, we are justified in concluding that it is true of all cases. When we say that all bodies attract one another, do we know this to be absolutely true? Certainly not. But we do know that, so far as those bodies are concerned which come under our observation, the statement is true, and we therefore have every reason to believe that it is true of all bodies.

**Combining Weights of the Elements.**—A careful study of the figures representing the composition of chemical compounds reveals a remarkable fact regarding the relative quantities of one and the same element which enter into combination with different elements. The proportions by weight in which some of the elements combine chemically are stated in the following table:

Sulphur,	1;	Iron,	7;	Iron,	7;
Oxygen,	1.	Oxygen,	2.	Sulphur,	4.
Magnesium,	3;	Tin,	59;	Zinc,	65;
Oxygen	2.	Oxygen,	16.	Oxygen,	16.

Tin,	59;	Zinc,	65;	Sodium,	23;
Sulphur,	16.	Sulphur,	32.	Oxygen,	8.
Sodium,	23;	Potassium,	39;	Potassium,	39;
Sulphur,	16.	Oxygen,	8.	Sulphur,	16.

We see that for iron, tin, zinc, sodium, and potassium the same figures are used, whether we are dealing with the compounds of these elements with oxygen or with sulphur. Now, if we were to determine the composition of all compounds which contain zinc, we should find that the relative quantity of zinc present could, in nearly all cases, be expressed by the figure 65. Similarly, the quantity of sodium could be expressed by the figure 23, and the quantity of potassium by 39. While in the compounds which iron forms with sulphur and oxygen the relative quantities of iron can be expressed by the figure 7, an examination of other compounds containing iron would show us that in order to express their composition we should frequently be obliged to use a larger number, and 56 is found to be the most convenient for the purpose. As with 7 parts of iron 2 parts of oxygen combine; so with 56 parts of iron 16 parts of oxygen combine; and with 56 parts of iron 32 parts of sulphur. A study of the compounds of oxygen shows that the number best adapted to expressing the relative quantities in which it occurs in its compounds is 16, and that for sulphur the most convenient number is 32. For every element a certain number can be selected, such that the proportions by weight in which this element enters into combination with others can be expressed by the number or by a simple multiple of it. These numbers express what are called the *combining weights*. It is not by any means an easy matter to determine which numbers are most convenient for all cases; and if the selection is to be determined solely by

convenience, there may be differences of opinion as to what is most convenient. We shall see a little later that, while the numbers primarily express the combining weights and nothing else, and are based solely upon determinations of the composition of chemical compounds, they have come to have a deeper significance and are now determined by methods which it would be premature to attempt to explain at this stage. The facts which it is of the highest importance that the student should understand now are:

- (1) That chemical action takes place between definite masses of substances; and
- (2) That the relative masses of the elements which enter into combination with one another can be expressed by numbers called the combining weights.

**Law of Multiple Proportion.**—The chief difficulty in the way of selecting a definite number for the combining weight of each element lies in the fact that two elements frequently combine in more than one set of proportions. Thus, while ordinarily iron and sulphur combine in the proportion 56 of iron to 32 of sulphur they also combine in the proportion 56 of iron to 64 of sulphur. Tin combines with oxygen in two proportions, forming two distinct compounds. In one 118 parts of tin are combined with 16 parts of oxygen; in the other 118 parts of tin are combined with 32 parts of oxygen. The elements potassium, chlorine, and oxygen combine in several proportions. In one compound there are 39 parts of potassium, 35.5 parts of chlorine, and 16 parts of oxygen; in a second, 39 parts of potassium, 35.5 parts of chlorine, and 32 parts of oxygen; in a third, 39 parts of potassium, 35.5 parts of chlorine, and 48 parts of oxygen; and in a fourth, 39 parts of potassium, 35.5 parts of chlorine, and 64 parts of oxygen. It will be

observed that while, in these compounds the quantities of oxygen and sulphur united with the same element or elements vary, these quantities are closely related to one another. In the case of iron and sulphur there is twice as much sulphur, relatively, in one compound as in the other. So, also, in the compounds of tin and oxygen, there is twice as much oxygen combined with a given quantity of tin in one case as in the other. Finally, in the four compounds which are made up of potassium, chlorine, and oxygen, the quantity of oxygen varies, being twice as great in the second compound as in the first, three times as great in the third, and four times as great in the fourth. These facts, and others of the same kind, are summed up in the *Law of Multiple Proportions*, which may be stated thus:

*If two elements, A and B, combine in different proportions, the relative quantities of B which combine with any fixed quantity of A bear a simple ratio to one another.*

The significance of the laws of definite and multiple proportions will scarcely be appreciated at this stage; but, as we go on, we shall see that they lie at the foundation of chemistry.

**Chemical Affinity.**—It is evident from what we have already learned that there is some power which can hold substances together in a very intimate way, so intimate that we cannot recognize them by ordinary means. We do not know what causes the sulphur and iron to combine, but we know that they do combine. Similarly, we do not know what causes a stone thrown in the air to fall back again, but we know that it falls back. It is true that we may say that the cause of the falling of the stone is the *attraction of gravitation*, but this does not give us any real information, for if we ask what the attraction of gravitation is,

we can only answer that it is that which causes all bodies to attract each other. We can also say, and do say, that the cause of the chemical union of substances is *chemical affinity*. But in so doing we are only giving a name to something about which we know nothing except the effects which it produces. All the chemical changes which are taking place around us may, then, be referred to the operation of chemical affinity. If this power were suddenly to cease to operate, what would be the result? Nature would be infinitely less complex than it now is. All substances now known to be *chemical compounds* would be resolved into the elements of which they are composed, and, as far as we know, there would be but about sixty or seventy different kinds of substances. All living things would cease to exist, and in their place we should have three invisible gases, and something very much like charcoal. Mountains would crumble to pieces, and all water would disappear, giving two invisible gases. The processes of life in its many forms would be impossible, as, however subtle that which we call life may be, we cannot imagine it to exist without the existence of certain complex forms of matter; and, as for the life process of larger animals and plants, most complex chemical changes are constantly taking place within them, and these changes are absolutely essential to the continuation of life. These considerations will suffice to show the great importance of the subject of chemistry, and how impossible it is without some knowledge of this subject to form any conception in regard to the most important phenomena of the universe.

**Summary.**—We have thus far learned the difference between *physical* and *chemical change*. We have learned the difference between *elements* and *chemical compounds*, and

between *chemical compounds* and *mechanical mixtures*. We have learned that there is a *close relation between the different kinds of physical change and chemical change*; and that one kind of change is capable of producing other kinds. We have learned how to distinguish chemical action from other kinds of action, the loss of their own properties which the substances suffer being a prominent characteristic of chemical action. And, finally, we have learned that the name chemical affinity is given to that which causes substances to act chemically upon one another, but that we do not know what chemical affinity is—we only know what effects it produces.

**How to Study Chemistry.**—We might learn a great deal about chemical facts and learn very little in regard to the *science* of chemistry. Science is organized knowledge. As long as we do not recognize any connection between any set of facts observed, or as long as only a few connections are recognized, we cannot properly speak of a subject as a science. The subject must have been studied for a long time. The laws governing the phenomena of the subject must have been discovered before that subject can be regarded as a science. Before we can have any conception of the science of chemistry we must become acquainted with some of the most important facts of the science, and we must also learn what connection exists between these facts. We must become familiar with substances, as they are, but especially with the way they act upon one another. Unfortunately for our purpose, but very few simple substances or elements occur in the uncombined form in nature. While, therefore, the simplest way to begin the study of chemical substances and chemical changes is by a consideration of the elements, the subject is com-

plicated by the fact that we cannot readily obtain these elements without the aid of substances which we have not studied and of processes which we cannot yet understand. There are, however, two elements which occur in nature in enormous quantities and which can be obtained in the uncombined condition very easily. As the kinds of action which they exhibit are of great importance and well calculated to give an insight into the nature of chemical action in general, we may profitably begin our study of chemical phenomena by a consideration of these two elements. They are oxygen and hydrogen. In learning the main facts in regard to these elements we shall learn a great deal that will be of importance in enabling us to understand other chemical phenomena; we shall begin to learn how to study things chemically; and shall thus prepare ourselves for a systematic study of the science of chemistry.

**The Elements and their Symbols.**—Before beginning this study a list of the elementary substances thus far discovered is here given. The names of those which are most widely distributed, and which form by far the largest part of the earth, are printed in small capitals. The names of those which are very rare are printed in italics. As was stated on page 13, not more than a dozen elements enter largely into the composition of the earth. These are the ones whose names are printed in small capitals. It has been calculated that the solid crust of the earth is made up approximately as represented in the subjoined table:

Oxygen,	44-48.7%	Calcium,	6.6-0.9%
Silicon,	22.8-36.2%	Magnesium,	2.7-0.1%
Aluminium,	9.9-6.1%	Sodium,	2.4-2.5%
Iron,	9.9-2.4%	Potassium,	1.7-3.1%

While oxygen forms a large proportion of the solid crust of the earth, it forms a still larger proportion (eight ninths)

of water by weight, and about one fifth of the air by volume. Carbon is the principal element entering into the structure of living things, while hydrogen, oxygen, and nitrogen also are essential constituents of animals and plants. Nitrogen forms about four fifths of the air by volume.

In representing the results of chemical action it is convenient to use abbreviations for the names of elements and compounds. Thus, instead of oxygen we may write simply O, for hydrogen H, for nitrogen N, etc., etc. These symbols are used in representing what takes place when substances act upon one another, as will be shown more clearly hereafter. Very frequently the first letter of the name of the element is used as the symbol. If the names of two or more elements begin with the same letter, this letter is used, but some other letter of the name is added. Thus, B is the symbol of boron, Ba of Barium, Bi of bismuth, etc. In some cases the symbol is derived from the Latin names of the elements. Thus, the symbol for iron is Fe, from Latin *ferrum*; for copper, Cu, from *cuprum*, for mercury, Hg, from *hydrargyrum*, etc. The symbols of the more common elements will soon become familiar by use. It is not desirable to attempt to commit them to memory at this stage.

The names themselves are derived from a variety of circumstances. Chlorine is derived from  $\chi\lambda\omega\rho\circ\varsigma$ , which means yellowish green, as this is the color of chlorine. Bromine comes from  $\beta\rho\tilde{\omega}\mu\circ\sigma$ , a stench, a prominent characteristic of bromine being its bad odor. Hydrogen comes from  $\tilde{\nu}\delta\omega\rho$ , water, and  $\gamma\acute{e}v\epsilon\iota\tau$ , to produce, signifying that it is a constituent of water. Similarly nitrogen comes from  $\gamma\iota\tau\rho\circ\tau$ , nitre, and  $\gamma\acute{e}v\epsilon\iota\tau$ , to produce, nitrogen being one of the constituents of nitre. Potassium is an element found in potash, and sodium is found in soda.

## LIST OF THE ELEMENTS AND THEIR SYMBOLS.

ALUMINIUM.....	Al	HYDROGEN.....	H	Ruthenium.....	Ru
Antimony.....	Sb	Indium.....	In	Samarium.....	Sm
Arsenic.....	As	Iodine.....	I	Scandium.....	Sc
Barium.....	Ba	Iridium.....	Ir	Selenium.....	Se
Bismuth.....	Bi	IRON.....	Fe	SILICON.....	Si
Boron.....	B	Lanthanum.....	La	Silver.....	Ag
Bromine.....	Br	Lead.....	Pb	SODIUM.....	Na
Cadmium.....	Cd	Lithium.....	Li	Strontium.....	Sr
Cesium.....	Cs	MAGNESIUM.....	Mg	Sulphur.....	S
CALCIUM.....	Ca	Manganese.....	Mn	Tantalum.....	Ta
CARBON.....	C	Mercury.....	Hg	Tellurium.....	Te
Cerium.....	Ce	Molybdenum.....	Mo	Thallium.....	Tl
CHLORINE.....	Cl	Niobium.....	Nb	Thorium.....	Th
Chromium.....	Cr	Nickel.....	Ni	Tin.....	Sn
Cobalt.....	Co	NITROGEN.....	N	Titanium.....	Ti
Columbium.....	Cb	Osmium.....	Os	Tungsten.....	W
Copper.....	Cu	OXYGEN.....	O	Uranium.....	U
Didymium.....	Di	Palladium.....	Pd	Vanadium.....	V
Erbium.....	E	Phosphorus.....	P	Ytterbium.....	Yt
Fluorine.....	F	Platinum.....	Pt	Yttrium.....	Y
Gallium.....	Ga	POTASSIUM.....	K	Zinc.....	Zn
Glucinum.....	Gl	Rhodium.....	Rh	Zirconium.....	Zr
Gold.....	Au	Rubidium.....	Rb		

## CHAPTER II.

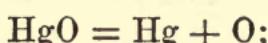
### CHEMICAL PHENOMENA PRESENTED BY OXYGEN.

IN Experiment 3 it was shown that when an electric current is passed through water two gases are liberated. One of these was distinguished by the readiness with which substances burned in it. This gas is oxygen. A gas with similar properties was also obtained by heating the red oxide of mercury. This is, in fact, the same substance.

**Occurrence of Oxygen.**—Oxygen is the most widely distributed element, and it occurs also in very large quantity. It has been stated that it forms between forty and fifty per cent of the solid crust of the earth, eight ninths of water, and about one fifth of the air.

**Preparation of Oxygen.**—The easiest way to make it is by heating some substance which contains it. The simplest example of this kind is that furnished by the oxide of mercury, which when heated yields mercury and oxygen. If the oxide be weighed, and, after decomposition, the oxygen and the mercury be weighed, the weight of the mercury plus the weight of the oxygen will be found to be equal to the weight of the oxide. Therefore the oxide contains only mercury and oxygen. They are chemically combined, and the heat overcomes the force which holds them together. We may represent the chemical compound

which contains mercury and oxygen by writing the symbols of the two elements side by side thus,  $\text{HgO}$ , which signifies primarily that the two elements are in chemical combination. If now we wish to represent what takes place when the oxide is heated, we can do so by means of an equation of this kind:



which should be read, Mercuric oxide gives mercury and oxygen.

Another substance which readily gives up oxygen when heated is potassium chlorate. This is a white crystallized substance, which is manufactured in large quantities. It contains the elements chlorine, oxygen, and potassium. When heated to a sufficiently high temperature it gives off all its oxygen, a compound of potassium and chlorine being left behind. The composition of potassium chlorate is represented by the formula  $\text{KClO}_3$ . This formula means, in the first place, that the substance contains potassium, chlorine, and oxygen in chemical combination. But as definite weights of the chemical elements combine, these symbols represent the definite weights. The symbol K means not only potassium, but it means 39 parts by weight of that element. The symbol Cl means 35.5 parts by weight of chlorine; and the symbol O stands for 16 parts by weight of oxygen. These figures, 39, 35.5, and 16, are the *combining weights* of the three elements (see page 25). The figure 3 written beneath the symbol O means that, in the compound represented, the quantity of oxygen present corresponds to three times its combining weight, or instead of 16 parts there are 48 parts of oxygen. The symbol  $\text{KClO}_3$ , then, means that the compound repre-

sented is made up of the three elements in the proportion potassium 39 parts, chlorine 35.5, oxygen 48 parts. If we were to analyze it we would find that its percentage composition is—

Potassium.....	31.84
Chlorine.....	28.98
Oxygen.....	39.18
	100.00

This is the invariable composition of the compound. If, therefore, we have a certain weight of the compound, it is an easy matter to calculate how much oxygen, or chlorine, or potassium it contains. Let it be required, for example, to calculate how much oxygen is contained in 4 grams of potassium chlorate. We know from the above that 39.18 per cent of potassium chlorate is oxygen, and as 39.18 per cent of 4 is 1.57, it follows that this is the weight of oxygen in the 4 grams. Or we may make the calculation thus: As potassium chlorate is made up of 39 parts of potassium, combined with 35.5 parts of chlorine and 48 parts of oxygen, in  $39 + 35.5 + 48 = 122.5$  parts of potassium chlorate we have 48 parts of oxygen. If in 122.5 parts there are 48 parts, how much is there in 4 grams? Plainly the answer is given by the solution of the simple proportion

$$122.5 : 48 :: 4 : x,$$

in which  $x$  represents the actual quantity of oxygen contained in 4 grams of potassium chlorate. Similarly the proportion

$$122.5 : 39 :: 4 : x$$

will give the quantity of potassium, and

$$122.5 : 35.5 :: 4 : x$$

will give the quantity of chlorine contained in 4 grams of potassium chlorate.

Let us now return to the preparation of oxygen. It has been found that when potassium chlorate is heated it gives off a gas, and this gas has been proved to be oxygen. This is in reality the most convenient method for making oxygen.

**EXPERIMENT 16.**—Arrange an apparatus as shown in Fig. 7. *A* represents a flask of 100 ccm. capacity. By means

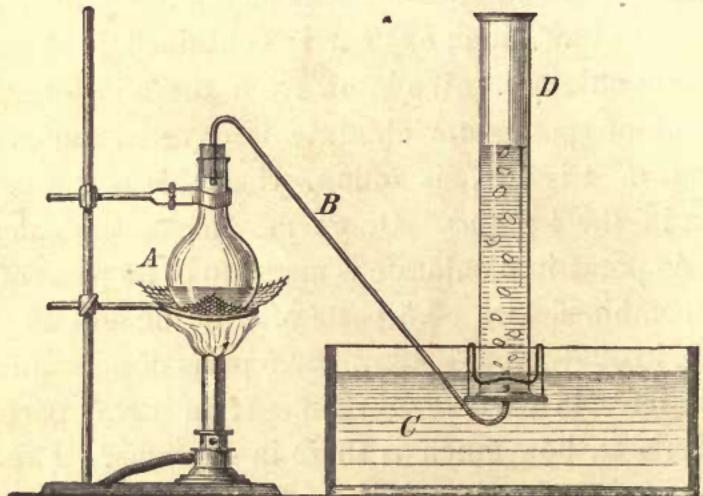


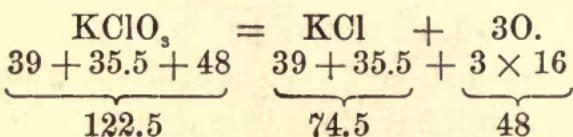
FIG. 7.

of a good-fitting rubber stopper one end of the bent glass tube *B* is connected with it, and the other end, which should turn upward slightly, is placed under the surface of the water in *C*. In *A* put 4 to 5 grams (about an eighth of an ounce) potassium chlorate, and gently heat by means of the lamp. Notice carefully what takes place. At first the potassium chlorate will melt, forming a clear liquid. If the heat be increased, the liquid will ap-

pear to boil, and it will soon be seen that a gas is being given off. Now bring the inverted cylinder D filled with water over the end of the tube, and let the bubbles of gas rise in the cylinder. After a considerable quantity of gas has been collected in this way the action stops, the mass in the flask becomes solid, and apparently the end of the process is reached. But if the heat be raised still higher, gas will again come off, and in this second stage a larger quantity will be collected than in the first. Finally, however, the end is reached, and the substance left in the flask remains unchanged, no matter how long heat may be applied. An examination of the gas collected will show that a piece of wood will burn in it very readily.

Now let us inquire exactly what has taken place in the experiment we have just performed. We started with a substance which contained the elements potassium, chlorine, and oxygen held together in chemical combination in certain definite proportions. We heated this, and thus effected the decomposition of the substance, the oxygen contained in it being set free. If we could examine the substance left behind in the flask, we should find that it contains no oxygen, but only potassium and chlorine in the proportions represented by the symbol KCl, *i.e.*, as we have seen, 39 parts of potassium to 35.5 parts of chlorine. For the chemist it is not a difficult operation to determine exactly what weight of this substance is left behind when a given weight of potassium chlorate is decomposed by heat, and exactly how much oxygen is given off in the decomposition. These determinations have been made over and over again, and the invariable result has been that, for every 122.5 parts of potassium chlorate decomposed,  $39 + 35.5 = 74.5$  parts of the compound KCl,

which is known as potassium chloride, are obtained, and 48 parts of oxygen given off. These are facts: there is no speculation involved in the statement. Now the facts can be conveniently represented by a chemical equation similar to that used to represent the decomposition of the oxide of mercury. The facts are that we start with 122.5 parts of potassium chlorate,  $\text{KClO}_3$ , and get 74.5 parts of potassium chloride,  $\text{KCl}$ , and 48 parts of oxygen. This is all represented by the equation:

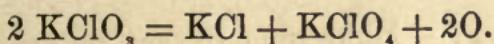


The figure 3 before the symbol of oxygen signifies that three times the combining weight of oxygen is represented. When the oxygen is in combination, as it is in potassium chlorate, the 3 is written below the line, as already explained.

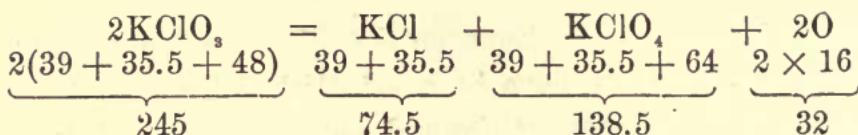
If, then, we know the combining weights of the elements, this equation conveys to our minds the idea of the decomposition of potassium chlorate into potassium chloride and oxygen by heat, and it also conveys to our minds the relations between the quantities of the substances represented. It is more convenient to use such a condensed expression than to state in words the facts which it represents, and hence constant use is made of similar expressions. It must be distinctly borne in mind that chemical equations are fundamentally different from mathematical equations. In mathematics if we have a very few simple ideas to start with we can construct a large number of equations which must be true if the ideas we start with are correct. Mathematical equations can be worked out in the

head. Chemical equations, on the other hand, simply represent facts which have been established by work in the laboratory. The quantities and nature of the substances must have been determined by some one, and the equation must be in accordance with what has actually been found.

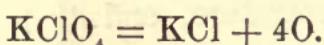
In the experiment we noticed a fact which is not taken account of in the equation. We noticed that the gas was given off in two stages: First, a part came off at a comparatively low temperature, and then a large quantity came off at a higher temperature. If we had measured the gas given off during the first stage, we would have found that it was only one third of the total obtained by complete decomposition. If, further, we had examined the solid substance left behind in the flask, we should have found that it consisted of two substances, one of which was potassium chloride,  $\text{KCl}$ , and the other a compound which contains more oxygen than the chlorate. The latter is called potassium perchlorate, and is represented by the formula  $\text{KClO}_4$ . The relative quantities of the two substances would also be found to correspond to the weights represented by the formulas  $\text{KCl}$  and  $\text{KClO}_4$ , *i.e.*, there would be found  $39 + 35.5 = 74.5$  parts of potassium chloride to  $39 + 35.5 + 4 \times 16 = 138.5$  parts of potassium perchlorate. To represent these facts we use the equation:



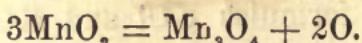
The figure 2 placed before the symbol for potassium chlorate,  $\text{KClO}_3$ , signifies that twice the combining weight of the compound takes part in the change, *i.e.*, twice the sum of the combining weights of the elements which enter into its composition. The quantitative relations represented are therefore:



In the second stage of the decomposition all the rest of the oxygen is given off, or, in other words, the potassium perchlorate is now decomposed. The quantities of oxygen and potassium chloride obtained are represented by the equation:



Another good method of preparing oxygen consists in heating black oxide of manganese. This is a black substance found in nature, called by mineralogists pyrolusite, and by chemists manganese dioxide. It consists of the elements manganese and oxygen in the proportions represented by the symbol  $\text{MnO}_2$ , the combining weight of manganese being 55. When this compound is heated it loses part of its oxygen, and there is left behind another compound of manganese and oxygen represented by the formula  $\text{Mn}_2\text{O}_4$ . The action is represented thus:



[PROBLEM.—How much oxygen can be obtained by heating 12 grams of manganese dioxide? How much manganese dioxide must be heated in order to get 3 grams of oxygen? In each case how much of the compound  $\text{Mn}_2\text{O}_4$  would be obtained?]

**EXPERIMENT 17.**—Make some oxygen by heating to redness 10 to 15 grams (about half an ounce) of manganese dioxide in an iron tube closed at one end and connected at the other end by means of a cork with a bent glass tube.

The most convenient way to make oxygen in the laboratory is to heat a mixture of equal parts of potassium chlo-

rate and manganese dioxide. This mixture gives off oxygen very readily with the aid of gentle heat. The potassium chlorate is alone decomposed under these circumstances, the manganese dioxide remaining unchanged; the part which it plays is not understood.

**EXPERIMENT 18.**—Mix 25 to 30 grams (or about an

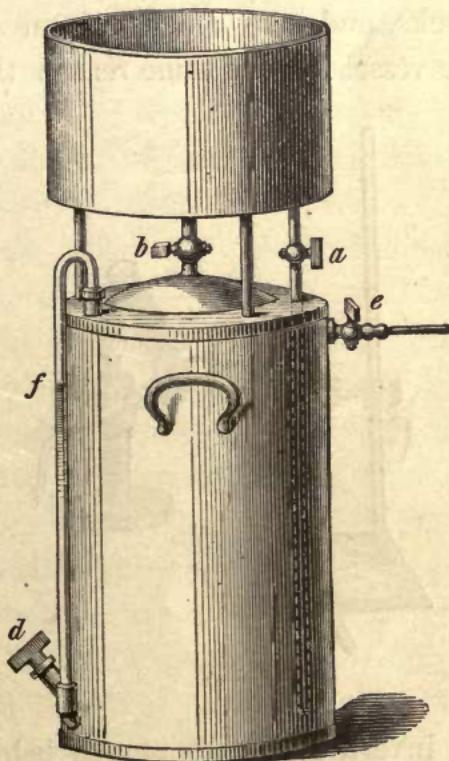


FIG. 8.

ounce) of potassium chlorate with an equal weight of manganese dioxide in a mortar. The substances need not be in the form of powder. Heat the mixture in a glass retort, and collect the gas by displacement of water in appropriate vessels,—cylinders, bell glasses, bottles with wide mouths, etc. It will also be well to collect some in a gasometer,

such as are commonly found in chemical laboratories, the essential features of which are represented in Fig. 8. It is made either of metal or of glass. The opening at *d* can be closed by means of a screw cap. In order to fill it with water open the stop-cocks and pour the water into the upper part of the vessel after having screwed the cap on to *d*. When it is full, water will flow out of the small tube *e*. Now close all the stop-cocks, and take the cap from *d*. The water will stay in the vessel for the same reason that it will stay

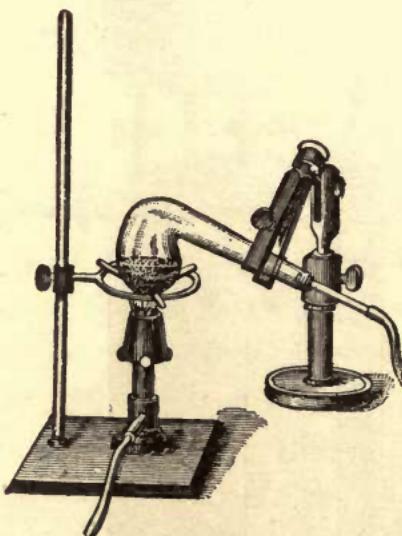


FIG. 9.

in the cylinder inverted with its mouth below water. To fill the gasometer with gas, put it over a tub or sink and introduce the tube from which gas is issuing into the opening at *d*. The gas will rise and displace the water, which will flow out at *d*. When full, put the cap on. We have now a supply of gas which we can draw upon as we may need it. To get the gas out of the gasometer, attach a rubber tube to *e*, pour water into the upper part of the gasometer, open the stop-cock *a* and that at *e*, when the

gas will flow out, and the current can be regulated by means of the stop-cock at *e*.

The arrangement of the retort is shown in Fig. 9.

**Physical Properties of Oxygen.**—Having thus learned how to get oxygen, we may proceed to study its properties. In the first place, the gas is invisible. The slight cloud which appears in the vessels when the gas is first collected is due to the presence of a very small quantity of a substance which is not oxygen. If the vessels are allowed to stand for a few minutes the cloud will disappear, and the vessels will look the same as if they were filled with air. The gas is tasteless and inodorous.

**EXPERIMENT 19.**—Inhale a little of the gas from one of the small bottles.

Oxygen is slightly heavier than the air. This can be determined by weighing a globe filled with air, then driving out the air by passing a current of oxygen through it for some time, and weighing it again. If these weighings are carefully made, it will be found that the relation between the weights of equal volumes of air and oxygen is 1 : 1.1056. Or, in other words, if a certain volume of air weighs 1 gram, the same volume of oxygen will weigh 1.1056 gram. When oxygen is subjected to very strong pressure and a very low temperature, it becomes liquid.

The properties of oxygen to which reference has thus far made are its *physical properties*. These are its appearance, taste, smell, relative weight, and changes in its condition, which still leave it in the elementary form uncombined chemically. Our knowledge of oxygen must, of course, include a knowledge of its physical properties, but, from the chemical standpoint, it is more important for us to know how oxygen acts chemically. What chemical changes

is it capable of bringing about? What conditions are necessary in order that it may act chemically? What laws govern the action? What products are formed?

**Chemical Conduct of Oxygen.**—In order to get an idea of the way in which oxygen acts upon some simple substances under ordinary circumstances, we may perform a few experiments.

**EXPERIMENT 20.**—Turn three of the bottles containing oxygen with the mouth upward, leaving them covered with glass plates. Into one introduce some sulphur in a so-called deflagrating-spoon, which is a small cup of iron or brass attached to a stout wire which passes through a round metal plate, usually of tin. (See Fig. 10.) In another put a little charcoal (carbon), and in a third a piece of phosphorus\* about the size of a pea. Let them stand quietly and notice what changes, if any, take place. Sulphur, carbon, and phosphorus are elements, and oxygen is an element. It will be noticed that the sulphur and the carbon remain unchanged, while some change is taking place in the vessel containing the phosphorus, as is shown by the appearance of white fumes. After some time the phosphorus will disappear entirely, the fumes will also disappear, and there will be nothing to show us what has become of the phosphorus. If the temperature of the room is rather high, it may happen that the phosphorus takes fire. If it should, it will burn with an intensely bright

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\* Phosphorus should be handled with great care. It is always kept under water, usually in the form of sticks. If a small piece is wanted, take out a stick with a pair of forceps, and put it under water in an evaporating-dish. *While it is under the water*, cut off a piece of the size wanted. Take this out by means of a pair of forceps, lay it for a moment on a piece of filter-paper, which will absorb most of the water; then quickly put it in the spoon.

light. After the burning has stopped, the vessel will be filled with white fumes, but these will quickly disappear, and the vessel will apparently be empty.

These experiments show us that oxygen does not act upon sulphur and carbon when brought in contact with them, and that the action upon phosphorus is generally slight. We might perform experiments of this kind with a great many substances, and we should reach the conclusion that at ordinary temperatures oxygen does not act upon substances. If, however, the substances be heated before they are introduced into the oxygen, the results will be entirely different. Instead of conducting itself as an inactive element, oxygen will act with great ease upon many substances. Things such as coal, wood, etc., which we know will burn in the air, burn in oxygen much more readily, and several substances such as iron, copper, etc., which will not burn in the air, burn in oxygen with ease.

**EXPERIMENT 21.**—In a deflagrating-spoon set fire to a little sulphur and let it burn in the air. Notice whether it burns with ease or with difficulty. Notice the odor of the fumes which are given off. Now set fire to another small portion and introduce it in a spoon into one of the vessels containing oxygen, as shown in Fig. 10. It will be seen that the sulphur burns much more readily in the oxygen than in the air. Notice the odor of the fumes given off. Is it the same as that noticed when the burning takes place in the air?



FIG. 10.

**EXPERIMENT 22.**—Perform similar experiments with charcoal.

**EXPERIMENT 23.**—Burn a *small* piece of phosphorus in the air and in oxygen. In the latter case the light emitted from the burning phosphorus is so intense that it is painful to some eyes to look at it. It is better to be cautious. The phenomenon is an extremely brilliant one. The walls of the vessel in which the burning takes place become covered with a white substance which afterwards gradually disappears.

What has taken place in these three experiments? In the first place, the substances were simply heated before being introduced into the oxygen. Nothing was added to them except heat. It is clear that while oxygen does not act upon these substances at ordinary temperatures, it does act upon them at higher temperatures. But what does the action consist in? We can determine this only by a careful study of the substances before and after the action. We must know not only what substances are brought together, *but also what weight* of each; and we must know what substances are left behind, and the exact weights of these. In the cases mentioned it would be a difficult matter for one not very thoroughly trained in the use of chemical methods to make all these determinations accurately, and unless they were made accurately they would fail to furnish us with the desired explanation. The determinations have fortunately been made so frequently that we cannot doubt what we should find were we to repeat them, and for the present we shall have to content ourselves with accepting the results, and we may use them as the basis of our reasoning. Something, however, we may learn for ourselves with but little difficulty. If in the experiment with sulphur we examine the spoon after the burning stops, we find that the sulphur has disappeared. We also notice that

there is present an invisible\* substance, which has a strong, disagreeable odor. This substance is not oxygen and it is not sulphur, but it is a gas which is formed by the burning of sulphur in oxygen. What has become of the oxygen? That it is no longer present in its original condition may be proved by introducing a burning stick into the vessel. Instead of continuing to burn with increased activity, as we have seen it do in oxygen, it is extinguished.

In the experiment with carbon the results are similar, only the invisible substance has no odor.

In the experiment with phosphorus the white substance which is deposited on the walls of the vessel is not phosphorus, as is clear from the fact that it dissolves in water. That the oxygen is used up when phosphorus acts on it may be shown by the following experiment:

**EXPERIMENT 24.** — Fill a tube say 30 to 40 cm. (12 to 15 inches) long, and  $2\frac{1}{2}$  to 3 cm. (1 to  $1\frac{1}{4}$  inches) wide, with oxygen, and arrange it in a vessel over water, as shown in Fig. 11. Now fasten a small stick of phosphorus to the end of a wire and push it into the tube so that about  $\frac{1}{4}$  to  $\frac{1}{2}$  inch of the phosphorus is above the water and exposed to the oxygen. At first no action will take place, but after a time white

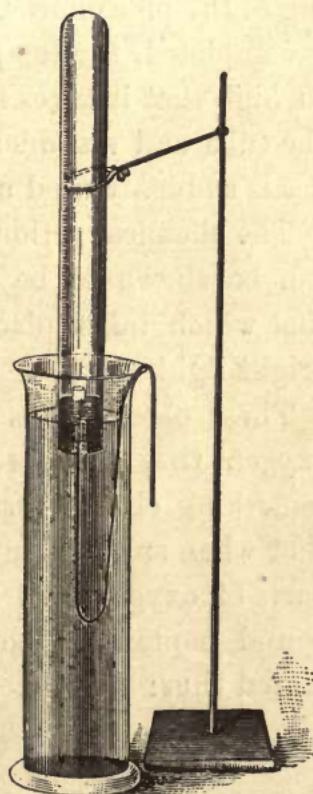


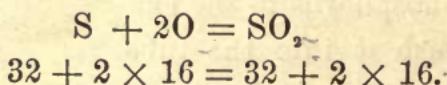
FIG. 11.

\* The fumes first noticed subside if a little water is in the bottle.

fumes will be seen to rise from the phosphorus, and the phosphorus will begin to melt. This action will be accompanied by a diminution of the volume of the oxygen, as will be shown by the rise of the water. When the water has risen so as to cover the phosphorus, shove the stick up so that it is again just above the surface of the water. Some of the oxygen will again be used up. By working carefully, and repeating this process as many times as may be necessary, the oxygen can all be used up without the active burning of the phosphorus. Usually, however, before the action is completed, the temperature of the phosphorus becomes so high that it takes fire, when there is a flash of light in the tube and a sudden rise of the water, showing that the gas is suddenly used up.

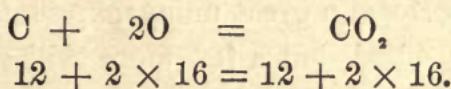
The chemical action, while the oxygen disappears slowly, can be shown to be essentially the same in character as that which takes place when the phosphorus burns with bright light.

These observations show that when substances burn in oxygen they disappear, the oxygen also disappears and something else is formed. Careful weighing has shown that when sulphur burns every 32 parts of sulphur use 32 parts of oxygen, and there are formed 64 parts of a compound containing both elements. The action is represented thus:



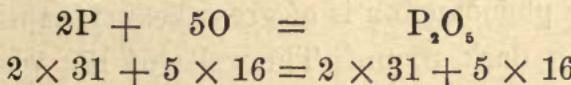
The compound represented by the formula  $SO_2$ , and known as sulphur dioxide, is the invisible substance which has the bad odor noticed. This is the only thing formed in the action,

In the case of carbon it has been shown that for every 12 parts of carbon burned 32 parts of oxygen disappear, and there are formed 44 parts of a compound containing both elements and represented by the formula  $\text{CO}_2$ . The equation representing the action is:



The compound  $\text{CO}_2$  is known as carbon dioxide. It is the invisible substance left behind in the vessel in which carbon burned in oxygen. It is the only thing found there, besides some carbon or oxygen which may have been present in excess of the quantities required for the action.

In the case of phosphorus, for every 62 parts of this element which disappear, 80 parts of oxygen are used up, and 142 parts of the compound  $\text{P}_2\text{O}_5$  are formed, as represented in the equation:



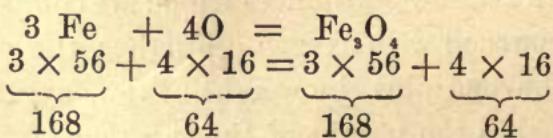
The compound  $\text{P}_2\text{O}_5$  is known as phosphorus pentoxide. It is the white substance found in the vessel.

In all three cases, then, the substances burned disappear, and at the same time a definite quantity of oxygen disappears and we get new substances which are compounds of the substances burned with oxygen. Further, the weight of the substance burned plus the weight of the oxygen used up is exactly equal to the weight of the substance formed. The oxygen, then, simply combines with the sulphur, the carbon, and the phosphorus. The union does not take place unless the temperature of the substances be raised somewhat before they are introduced into the oxygen. The act of combina-

tion is accompanied by an evolution of light and heat. These, however, are secondary. They result from the rapid coming-together of the particles of the two elements, caused by chemical attraction, just as a bullet is heated by being rapidly projected against a hard target which stops it.

We might perform a great many experiments similar to those already studied, but a few more will suffice.

**EXPERIMENT 25.**—Straighten a steel watch-spring\* and fasten it in a piece of metal, such as is used for fixing a deflagrating-spoon in an upright position; wind a little thread around the lower end, and dip it in melted sulphur. Set fire to this and insert it into a vessel containing oxygen. For a moment the sulphur will burn as in Experiment 21; but soon the steel begins to burn brilliantly, and the burning continues as long as there is oxygen left in the vessel. Notice that in this case *there is no flame*, but instead very hot particles are given off from the burning iron. The phenomenon is of great beauty, especially if observed in a dark room. The walls of the vessel become covered with a dark reddish-brown substance, some of which will also be found at the bottom in larger pieces. This substance is a compound of iron and oxygen known as magnetic oxide of iron, and represented by the formula  $\text{Fe}_3\text{O}_4$ . The action is represented by the equation :



The reason why no flame is observed in the burning of iron is that the substance formed is a solid and not a gas.

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\* Old watch-springs can generally be had of any watch maker or mender for the asking.

What we call a *flame* is either a gas burning or any substance burning and forming a gaseous product. When sulphur burns it forms a gaseous product, and is itself converted into gas before it burns. It burns with a flame. When carbon burns the product is a gas. It burns with a slight flame.

**Burning in the Air.**—We cannot well help noticing a strong resemblance between the burning of substances in oxygen and in the air, and the question naturally suggests itself, Are these two acts the same? Or is there a difference between them? To answer these questions, we must burn the same things in pure oxygen and in air, and see whether the same product is formed in each case, and at the same time whether anything else is formed? If we should make this comparison in any case we should find that whether a substance burns in the air or in pure oxygen the same product is formed, and nothing else. It is therefore certain that the act of burning in the air is due to the presence of oxygen. We shall learn later that the reason why substances do not burn as readily in the air as in pure oxygen is that in the air there is present a large quantity of another gas which does not act upon the substances at all.

**Combustion.**—By the term combustion in its broadest sense is meant any chemical act which is accompanied by an evolution of light and heat. Ordinarily, however, it is restricted to the union of substances with oxygen as this union takes place in the air, with evolution of light and heat. Substances which have the power to unite with oxygen are said to be *combustible*, and substances which have not this power are said to be *incombustible*. Most elements combine with oxygen under proper conditions, and are therefore combustible. Most compounds formed by the union of

oxygen with combustible substances are incombustible. For example, the sulphur dioxide, carbon dioxide, and phosphorus pentoxide obtained in Experiments 21, 22, and 23 are incombustible. They contain oxygen, and they cannot directly combine with any more.

**Kindling Temperature.**—We have seen that substances do not usually combine with oxygen at ordinary temperatures, but that in order to effect the union the temperature must be raised. If this were not the case, it is plain that every combustible substance in nature would burn up, for the air supplies a sufficient quantity of oxygen for this purpose. Some substances need to be heated to a high temperature before they will combine with oxygen; others require but very slight elevation. If we were to subject a piece of phosphorus, of sulphur, and of carbon to the same gradual rise in temperature, we would find that the phosphorus takes fire very easily, only a slight elevation of temperature being necessary; next in order would come the sulphur, and last the carbon. If we were to repeat these experiments a number of times, we should find that the phosphorus would always take fire at the same temperature, and a similar result would be reached in the cases of sulphur and carbon. Every combustible substance has its kindling temperature; that is, the temperature at which it will unite with oxygen. Below this temperature it will not unite with oxygen. If a piece of wood could be heated to its kindling temperature all at once, it would burn up as rapidly as it could secure the necessary oxygen; but the burning does not usually take place rapidly, for the reason that only a small part of it is at any one time heated to the kindling temperature. Watch a stick of wood burning, and watch how, as we say, “the fire creeps” slowly along it. The reason

of the slow advance is simply this: only those parts of the stick which are nearest the burning part become heated to the kindling temperature. They take fire and heat the parts nearest them, and so on gradually throughout the length of the stick.

**Slow Oxidation.**—Substances may combine slowly with oxygen without evolution of light. Thus, if a piece of iron be allowed to lie in moist air, it becomes covered with rust. This rust is similar to the substance formed when iron is burned in oxygen. Both are formed by the union of iron and oxygen. Magnesium burns in the air, as we have seen, and forms a white compound containing oxygen. It burns with increased brilliancy in oxygen, forming the same compound. If left in moist air for some days or weeks, it becomes covered with a layer of the same white substance. If this be scraped off and the magnesium again allowed to lie, it will again become covered with a layer of the compound with oxygen, and this may be continued until the magnesium has been completely converted into the same substance that is formed when it burns in oxygen or in the air. Many other similar cases of slow oxidation might be described, some of which, such as the decay of wood, are constantly taking place in nature. The most important illustration of slow oxidation is that which takes place in our bodies, for, as we shall see, the food which we partake of undergoes a great many changes; some of the substances uniting with oxygen, and thus keeping up the temperature of our bodies. This, however, is done without evolution of light and without apparent evolution of heat.

We take large quantities of oxygen into our lungs in breathing. This acts upon various substances presented to it, oxidizing them to other forms which can easily be got

rid of. More will be said in regard to the breathing process of animals and plants when the subject of carbon and its compounds with oxygen is considered.

**Heat of Combustion.**—What is the chief difference between combustion, as we ordinarily understand it, and slow oxidation? So far as we can judge by a cursory examination, it is that in the former there is an evolution of light and heat, and in the latter there is not. Remembering that the reason why a body gives light is that it is heated to a sufficiently high temperature, the problem resolves itself into a question of heat. What difference, if any, is there between the quantity of heat given off when a substance burns and when it undergoes slow oxidation without evolution of light? The answer is of the highest importance. *There is no difference whatever.* In one case the heat is all given off in a short space of time, and therefore the temperature of the substance becomes high and it emits light. In the other the heat is given off slowly and continues for a much longer time, and therefore the temperature of the substance does not get very high, as surrounding substances conduct off the heat as rapidly as it is evolved. If, however, we were to measure the *quantity* of the heat, we would find it to be the same in both cases.

We may measure the quantity of heat given off in a chemical reaction by allowing the reaction to take place in a vessel called a calorimeter, so constructed as to prevent loss of heat, and containing a known weight of water. The temperature of the water is noted at the beginning of the operation and at the end. A quantity of heat is generally stated by giving the number of grams of water which it will raise one degree Centigrade in temperature. The quantity of heat necessary to raise a gram of water one de-

gree (Centigrade) in temperature is the unit used in heat measurement. It is called the calorie. If, therefore, we say the quantity of heat evolved in any reaction is 250 calories (written generally 250 cal.), we mean simply a quantity of heat which would raise the temperature of 250 grams of water one degree (Centigrade) in temperature.

To repeat, then: by the heat of combustion of a substance we mean simply the quantity of heat given off when a certain weight of the substance combines with oxygen. In order to avoid confusion it is necessary to have an agreement in regard to the weight of substance which shall be used as the standard. This may be a gram or any other weight, but for the purposes of chemistry it is most convenient to take weights in proportion to the combining weights. Thus, by the heat of combustion of carbon is meant the quantity of heat evolved by the combination of 12 grams of carbon with  $2 \times 16 = 32$  grams of oxygen. By the heat of combustion of sulphur is meant the quantity of heat evolved in the combination of 32 grams of sulphur with  $2 \times 16 = 32$  grams of oxygen, etc.

It will be found that not only is the heat of combustion a fixed quantity whether the union with oxygen takes place slowly or rapidly, but that the heat evolved in any given chemical reaction is always the same, and that chemical combination is always accompanied by an evolution of heat.

**Heat of Decomposition.**—Just as it is true that a definite quantity of heat is evolved when two or more elements combine chemically, so also it is true that in order to overcome the force which holds these elements together the same quantity of heat is absorbed. Thus the heat of formation of the oxide of mercury is 30,660 cal.; or, in other

words, when 200 grams of metallic mercury and 16 grams of oxygen combine, 30,660 calories are evolved. Now, we have seen that when heat is applied to the compound it is decomposed into its elements. To effect this decomposition, as much heat is absorbed as was evolved in the formation.

**Chemical Energy and Chemical Work.**—Any substance which has the power to unite with others can do *chemical work*, it possesses *chemical energy*. Thus, all combustible substances can do work. In uniting with oxygen heat is evolved, and this can be transformed into motion. To go back to the example of the steam-engine, which was referred to in an early part of the book, the cause of the motion is the burning of the fuel. We thus see that the source of the power in the steam-engine is chemical energy. Substances which have not the power to combine with others have no power to do chemical work, or they have no chemical energy. As far as power to combine with oxygen is concerned, water is a substance of this kind, as is also carbon dioxide, the gas formed when carbon is burned in oxygen. In order that they may do work, they must first be decomposed and their constituents put together in some form in which they have the power of combination. This decomposition of carbon dioxide and water is taking place constantly on the earth. All plant-life is dependent on it. The products of the action, *i.e.*, the different kinds of wood, have energy,—they can do chemical work. This power to do work has been acquired from the heat of the sun, to which the decomposition of the carbon dioxide and water is mainly due. We have thus a transformation of the sun's heat into chemical energy, which is stored up in the combustible woods. The quantity of heat which

would be given off in burning the wood would be exactly equal to the quantity used up in its formation.

**Oxides.**—The compounds of oxygen with other elements are called *oxides*. To distinguish between different oxides the name of the element with which the oxygen is in combination is prefixed. Thus the compound of zinc and oxygen is called zinc oxide ; that of calcium and oxygen, calcium oxide ; that of silver and oxygen, silver oxide, etc. When an element forms more than one compound with oxygen, suffixes are made use of to distinguish between them. Thus in the case of copper there are two oxides which have the formulas  $Cu_2O$  and  $CuO$ . The former is known as *cuprous oxide* and the latter as *cupric oxide*. That oxide which contains the smaller proportion of oxygen in combination with any fixed quantity of the other element is designated by the suffix *ous*, that which contains the larger proportion of oxygen is designated by the suffix *ic*. In other cases the number of combining weights of oxygen contained in the compound is indicated by the name. Thus manganese dioxide is  $MnO_2$ ; sulphur trioxide is  $SO_3$ , etc.

## CHAPTER III.

### HYDROGEN.

IN Experiment 3 it was found that when an electric current is passed through water two gases are obtained, one of which we have since studied and found to be oxygen. The other, it will be remembered, takes fire and burns, and is thus easily distinguished from oxygen. This second gas is hydrogen, which we may now proceed to study.

**Occurrence.**—Hydrogen is found in nature very widely distributed, and in large quantity. It forms one-ninth the weight of water, and is contained in all substances which enter into the composition of plants and animals.

**Preparation of Hydrogen.**—It may be prepared:

(a) By decomposition of water by means of the electric current;

(b) By decomposition of water by the action of certain metals;

(c) By the action of substances known as acids on metals.

The following experiments will illustrate these methods:

**EXPERIMENT 26.**—Repeat Experiment 3 and examine the gases.

**EXPERIMENT 27.**—Throw a small piece of sodium\* on

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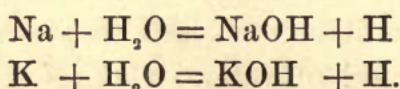
\* The metals sodium and potassium are kept under oil. When a small piece is wanted take out one of the larger pieces from the bottle, roughly wipe off the oil with filter paper and cut off a piece the size needed. It is not advisable to use a piece larger than a pea.

water. While it is floating on the surface apply a lighted match to it. A yellow flame will appear. This is burning hydrogen, the flame being colored yellow by the presence of the sodium, some of which also burns. Make the same experiment with potassium. The flame appears in this case without the aid of the match. It has a violet color which is due to the burning of some of the potassium. The gas given off in these experiments is either burned at once or escapes into the air. In the case of the potassium the action takes place rapidly, and the heat evolved is sufficient to set fire to the gas. In the case of the sodium the heat evolved does not set fire to the gas. In order to collect it unburned, it is only necessary to allow the decomposition to take place, so that the gas will rise in an inverted vessel filled with water. For this purpose fill a good-sized test-tube with water and invert it in a vessel of water. Cut off a piece of sodium not larger than a pea, wrap it in a layer or two of filter paper, and with the fingers or a pair of curved forceps bring it quickly below the mouth of the test-tube and let go of it. It will rise to the top, the decomposition of the water will take place quietly, and the gas formed, being unable to escape, will remain in the tube. By repeating this operation in the same tube a second portion of gas may be made, and so on until enough has been made.

Examine the gas and see whether it acts like the hydrogen obtained from water by means of the electric current. What evidence have you that they are the same? Is this evidence sufficient to prove the identity of the two?

The metals sodium and potassium disappear in these experiments, and we get hydrogen. What becomes of the metals? and what is the source of the hydrogen? If after the action has stopped the water be examined, it will be

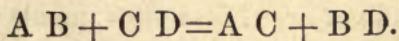
found to contain something in solution. It now has a peculiar taste which we call alkaline; it feels slightly soapy to the touch; it changes certain vegetable colors. If the water is evaporated off, a white substance remains behind which is plainly neither sodium nor potassium. In solid form or in very concentrated solution it acts very strongly on animal and vegetable substances, disintegrating many of them. On account of this action it is known as *caustic* soda, or, in the case of potassium, as *caustic* potassa. Analysis has shown that they are made up as represented by the formulas NaOH and KOH. From any given quantity of water decomposed, only half the hydrogen is given off. The action is represented by the equations:



As will be shown, the composition of water is represented by the formula H<sub>2</sub>O. The hydrogen and oxygen are held together by chemical affinity, as we say. Now, if anything is brought in contact with the water which has a stronger affinity for oxygen than hydrogen has, the water will be decomposed, and the hydrogen will give way to the new substance. This is what takes place in the case of sodium and potassium. These metals have a stronger affinity for oxygen than hydrogen has, and therefore they displace a part of the hydrogen when a compound is formed which is so stable that it is not decomposed by the metals.

**Chemical Action Caused by Differences between the Attractions of the Elements for One Another.**—We have seen that chemical action can be effected by means of heat and electricity; and also that when certain elements are brought together the attraction which they have for one another causes

them to combine directly, as in the case of phosphorus and oxygen. By far the largest number of chemical reactions, however, which we have to deal with are the result of bringing together two or more chemical compounds, the constituents of which rearrange themselves in the form of new compounds in accordance with the strength of the attractions of the constituents. Thus, if we have two compounds one of which is made up of the elements A and B and another made up of C and D, and the attraction of A for C is greater than that of A for B or C for D, and, at the same time, B and D have an attraction for each other, then, on bringing together the compounds A B and C D a reaction will take place thus :



There are various conditions which may modify this law, but these will be readily understood by the aid of examples which will soon present themselves.

**EXPERIMENT 28.**—Certain metals which do not decompose

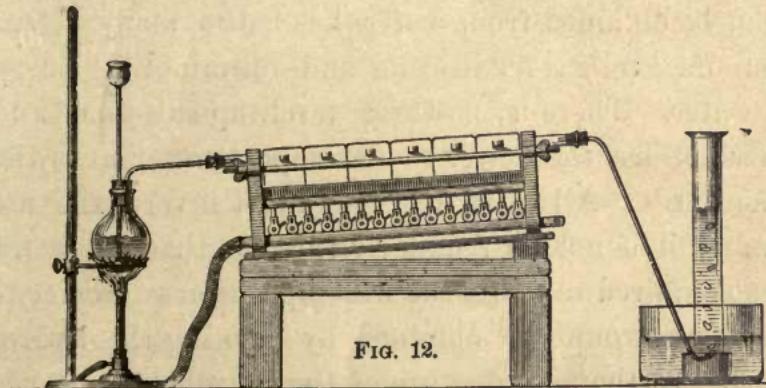
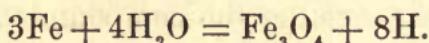


FIG. 12.

water at ordinary temperatures, or which decompose it slowly, decompose it easily at elevated temperatures. This is true of iron. If steam be passed through a tube containing pieces of iron heated to redness, decomposition of the water takes

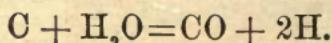
place, the oxygen is retained by the iron, which enters into combination with it, while the hydrogen is liberated. In this experiment a porcelain tube with an internal diameter of from 20 to 25 mm. (about an inch) and a gas furnace are desirable, though a hard glass tube and a charcoal furnace will answer. The arrangement of the apparatus is shown in Fig. 12.

The hydrogen may be collected by displacement of water, as in the case of oxygen. The reaction which takes place is represented thus :



**PROBLEMS.**—How much water could be decomposed by 20 kilograms (or 40 pounds) of iron? and how much would the hydrogen obtained weigh? one litre of hydrogen at 0° C. and under the normal atmospheric pressure of 760 mm. weighs 0.089578 gram. What will be the volume of hydrogen obtained by using up 20 kilograms of iron in the decomposition of water?

Many other substances have the power to decompose water and set hydrogen free. The fact that a combustible gas can be obtained from water has led to many attempts to manufacture gas for heating and illuminating purposes from water. There is, however, no cheap substance known to us which has the power to decompose water at ordinary temperatures. All other methods must involve the use of heat, and it is not unfrequently the case that the quantity of heat required to effect the decomposition is greater than that which would be obtained by burning the hydrogen formed. In the manufacture of the so-called "water gas" which is now extensively used in the United States both for illuminating and heating purposes, water is decomposed by means of carbon which is used in the form of hard coal. The reaction takes place mainly according to this equation:



Both products are gases, and both burn; and when this mixture is enriched by some of the oils obtained from petroleum, it burns well and gives a good light.

By far the most convenient method for making hydrogen consists in treating a metal with an acid. As will be seen later, acids are substances which contain hydrogen, and which are characterized by the fact that they give up this hydrogen very easily and take up other elements in the place of it. Among the common acids found in every laboratory are *hydrochloric acid*, *sulphuric acid*, and *nitric acid*. The chemistry of these compounds will be considered in due time; but as we shall be obliged to use them before they are studied systematically, a few words in regard to them are desirable at this time.

*Hydrochloric acid* is a compound of hydrogen and chlorine. It is a gas which dissolves easily in water. It is this solution which we use in the laboratory, and which is manufactured in enormous quantities in connection with the manufacture of soda or sodium carbonate. Its chemical formula is HCl. It is frequently called "Muriatic acid."

*Sulphuric acid* is a compound of sulphur, oxygen, and hydrogen in the proportions represented by the formula  $H_2SO_4$ . It is an oily liquid and is frequently called "Oil of Vitriol." It is manufactured in very large quantities, as it plays an important part in many of the most important chemical industries.

*Nitric acid* is a compound containing nitrogen, oxygen, and hydrogen in the proportions represented in the formula  $HNO_3$ . It is a colorless liquid, though as we get it it is commonly colored somewhat yellow.

When a metal, as zinc, is brought in contact with hydrochloric or sulphuric acid, an evolution of gas takes place at once.

**EXPERIMENT 29.**—In a cylinder or test-tube put some small pieces of zinc, and pour upon it some ordinary hydrochloric acid. After the action has continued for a minute or two apply a lighted match to the mouth of the vessel. The gas will take fire and burn. If sulphuric acid diluted with five or six times its volume of water\* be used in-

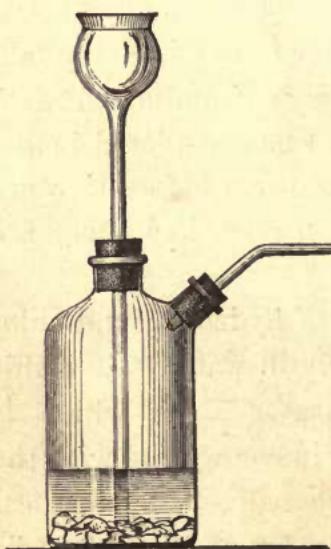


FIG. 13.



FIG. 14.

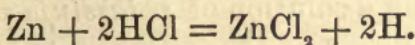
stead of hydrochloric acid, the same result will be reached. The gas evolved is hydrogen. For the purpose of collecting the gas the operation is best performed in a bottle with two necks called a Wolff's flask (see Fig. 13), or in a wide-mouthed bottle in which is fitted a cork with two holes (see Fig. 14). Through one of the holes passes a funnel-

\* If it is desired to dilute ordinary concentrated sulphuric acid with water, the acid should be poured slowly into the water while the mixture is constantly stirred. If the water is poured into the acid, the heat evolved at the places where the two come in contact may be so great as to convert the water into steam and cause the strong acid to spatter.

tube, and through the other a glass tube bent in a convenient form.

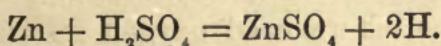
The zinc used is usually what is known as granulated zinc. It is prepared by melting it in a ladle and pouring the molten metal from an elevation of four or five feet into water. The advantage of this form is that it presents a large surface to the action of the acids. A handful of this zinc is introduced into the bottle, and enough of a *cooled* mixture of sulphuric acid and water (1 volume concentrated acid to 6 volumes water) poured upon it to cover it. Usually a brisk evolution of gas takes place at once. Wait for two or three minutes, and then collect some of the gas by displacement of water. When the action becomes slow, add more of the dilute acid. It will be well to fill several cylinders and bottles with the gas, and also a gasometer, from which it can be taken as it is needed for experiments.

The action which takes place in the case of zinc and hydrochloric acid is represented thus :



The compound  $\text{ZnCl}_2$  is called zinc chloride. It is left in solution in the vessel. If there is sufficient zinc present, all the hydrochloric acid will be changed in accordance with the above equation.

In the case of sulphuric acid and zinc the action is represented thus :



The compound  $\text{ZnSO}_4$  is called zinc sulphate. It is the substance commonly known as white vitriol. It is in solution in the flask, and can be obtained by evaporating off the water.

**EXPERIMENT 30.**—After the action is over pour the contents of the flask through a filter into an evaporating-dish, and boil off the greater part of the water, so that, on cooling, the substance contained in solution will be deposited. If the operation is carried on properly, the substance will be deposited in regular forms called crystals. It is zinc sulphate,  $ZnSO_4$ , formed by the replacement of the hydrogen of the sulphuric acid by zinc.

**PROBLEMS.**—How much zinc would it take to give 200 litres of hydrogen? How much zinc sulphate would be formed? How much hydrogen would be formed by the action of 50 grams of zinc on sulphuric acid? How much sulphuric acid would be used up? The combining weight of zinc is 65.

**Physical Properties of Hydrogen.**—Hydrogen is a colorless, inodorous, tasteless gas. Made by the action of zinc on acids, it has a slightly disagreeable odor. This is due to the presence of impurities. If it be passed through certain substances which have the power to destroy the impurities, the odor is destroyed.

**EXPERIMENT 31.**—Pass some of the gas through a wash cylinder containing a solution of *potassium permanganate*; collect some of it, and notice whether it has an odor or not. The apparatus should be arranged as shown in Fig. 15. The solution of potassium permanganate is, of course, contained in the small cylinder *A*, and the tubes so arranged that the gas bubbles through it.

The gas is not poisonous, and may therefore be inhaled with impunity. We could not, however, live in an atmosphere of hydrogen, as we need oxygen. It is the lightest known substance, being fourteen and a half times lighter than the air and sixteen times lighter than oxygen. Its lightness may be shown by a number of simple experiments.

**EXPERIMENT 32.**—Place a vessel containing hydrogen with the mouth upward and uncovered. In a short time examine the gas, and see whether it is hydrogen.

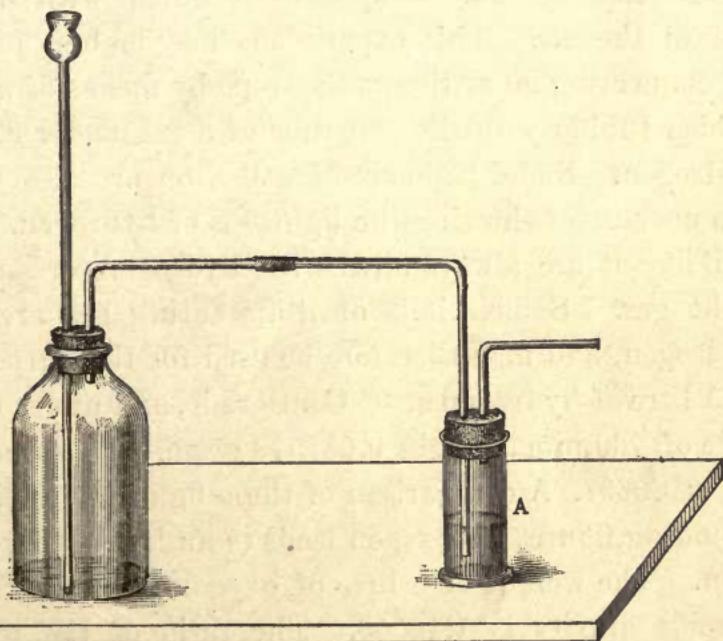


FIG. 15.

**EXPERIMENT 33.**—Gradually bring a vessel containing hydrogen with its mouth upward below an inverted vessel



FIG. 16.

containing air, in the way shown in Fig. 16. The air will be displaced. On examination, the inverted vessel will be

found to contain hydrogen, while the one with the mouth upward will contain none. The gas is thus poured upwards.

**EXPERIMENT 34.**—Soap-bubbles filled with hydrogen rise in the air. This experiment may be best performed by connecting an ordinary clay pipe by means of a piece of rubber tubing with the exit-tube of a gasometer filled with hydrogen. Small balloons of collodion are also made for the purpose of showing the lightness of hydrogen.

Balloons are always filled with hydrogen, or some other light gas. Some kinds of illuminating gas are rich in hydrogen, and may therefore be used for the purpose.

A litre of hydrogen at 0° Centigrade, and under the pressure of 760 mm., weighs 0.089578 gram. Its specific gravity is 0.0691. A comparison of these figures with the corresponding figures for oxygen leads to an interesting observation. The weight of a litre of oxygen is 1.429 grams; its specific gravity is 1.10563. The ratio of the weight of equal volumes of hydrogen and oxygen to each other is 1 : 16, or

$$0.089578 : 1.429 :: 1 : 16.$$

But the figures 1 and 16 are the combining weights of these elements; that is to say, they are the figures best adapted to expressing the relative quantities of these elements which enter into combination. There appears, therefore, to be a close connection between the absolute weights of equal volumes of these gases and the figures representing their combining weights. We shall see that this connection is observed between the weights of other gases; the explanation, however, had better be postponed until some other facts, the knowledge of which is necessary in

order to make the explanation intelligible, shall have been considered.

When subjected to a very low temperature and high pressure hydrogen becomes liquid.

**Chemical Properties of Hydrogen.**—Under ordinary circumstances, hydrogen is not a particularly active element. It does not unite with oxygen at ordinary temperatures, but, like wood and most other combustible substances, needs to be heated up to the kindling temperature before it will burn. We have seen that it burns if a lighted match be applied to it. The flame is colorless, or very slightly blue. As burned under ordinary circumstances, the flame is colored, in consequence of the presence of foreign substances; but that it is colorless when the gas is burned alone can be shown by burning it from a platinum tube, which is itself not acted upon by the heat.

**EXPERIMENT 35.**—If there is no small platinum tube available, roll up a small piece of platinum foil and melt it into the end of a glass tube, as shown in Fig. 17. Connect the burner thus made with the gasometer containing hydrogen, and after the gas has been allowed to issue from it for a moment, set fire to it. In a short time it will be seen that the flame is practically colorless, and gives no light.



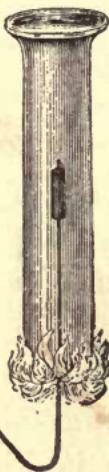
FIG. 17.

That it is hot can be readily shown by holding a piece of platinum wire or a piece of some other metal in it.

Hydrogen burns. We have seen that this consists in combining with oxygen. On the other hand, substances which burn in the air are extinguished when put in a vessel containing hydrogen. This is equivalent to saying that a

body which is uniting with oxygen does not continue to unite with oxygen when put in an atmosphere of hydrogen, and does not combine with the hydrogen. This is expressed by saying that hydrogen does not support combustion. The following experiment shows this.

**EXPERIMENT 36.**—Hold a cylinder filled with hydrogen with the mouth downward. Insert into the vessel a lighted taper held on a bent wire, as shown in Fig. 18. The gas



takes fire at the mouth of the vessel, but the taper is extinguished. On withdrawing the taper and holding the wick for a moment in the burning hydrogen, it will take fire, but on putting it back in the hydrogen it will again be extinguished. Other burning substances should be tried in a similar way.

As when hydrogen burns it combines with oxygen, a product should be obtained in which both hydrogen and oxygen are present. In the experiments performed we have seen no evidence of the formation of such a product, simply for the reason that when formed it is an invisible gas, and, though it can easily be condensed to a liquid, no precautions were taken to get it in this form. The product is, in fact, ordinary water, which we will next study.

## CHAPTER IV.

### COMBINATION OF HYDROGEN AND OXYGEN.—WATER.

WATER was long regarded as an element until, towards the end of last century, the discovery of hydrogen and oxygen, and of the nature of combustion, led to the discovery of its true composition.

**Occurrence.**—The wide distribution of water on the earth is familiar to every one. But water also occurs in forms and conditions which prevent its immediate recognition. Thus all living things contain a large proportion of water, which can be driven off by heat. If a piece of wood or a piece of meat be heated, water passes off.

**EXPERIMENT 37.**—In a dry tube heat gently a small piece of wood. What evidence do you obtain that water is given off? Do the same thing with a piece of fresh meat.

The proportion of water in animal and vegetable substances is very great. If the body of a man weighing 150 pounds were to be put in an oven and thoroughly dried, there would be left only about 40 pounds of solid matter, all the rest being water. As all meat, vegetables, and food-stuffs in general contain a similar large proportion of water, it is evident that water is a very important article of commerce. When we buy four pounds of beef, we pay for about three pounds of water and one of solid matter.

Water also occurs in another form in which it does not

easily reveal its presence. This is as *water of crystallization*.

**EXPERIMENT 38.**—Take some of the crystals of zinc sulphate obtained in Experiment 31. Spread them out on a layer of filter paper, and finally press two or three of them between folds of the paper. Examine them carefully. They appear to be quite dry, and in the ordinary sense they are dry. Put them in a dry tube, and heat them gently, when it will be observed that water condenses in the upper part of the tube, while the crystals lose their lustre, becoming white and opaque, and at last crumbling to powder.

**EXPERIMENT 39.**—Perform a similar experiment with some gypsum, which is the natural substance from which “Plaster of Paris” is made.

**EXPERIMENT 40.**—Heat a few small crystals of copper sulphate or blue vitriol. In this case the loss of water is accompanied by a loss of color. After all the water is driven off, the powder left behind is white. On dissolving it in water, however, the solution will be seen to be blue; and if the solution be evaporated until the substance is deposited, it will appear in the form of blue crystals.

Many compounds when deposited from solutions in water in the form of crystals combine with definite quantities of water. This water is not present as such, but is held in chemical combination. Hence the substance does not appear moist, though it may contain more than half its weight of water. This water of crystallization is, in some way which we do not understand, essential to the form of the crystal. If it is driven off by heat, the crystal is destroyed. Some compounds combine under different circumstances with different quantities of water, the form of the crystals varying with the quantity of water in combination.

Compounds differ greatly as regards the ease with which they give up water of crystallization. In general, it is given off when the compound containing it is heated to the temperature of boiling water. But some compounds give it up by simple contact with the air. This is true of sodium sulphate, or Glauber's salt, which contains a quantity of water of crystallization represented by the formula  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .

**EXPERIMENT 41.**—Select a few crystals of sodium sulphate which have not lost their lustre. Put them on a watch-glass, and let them lie exposed to the air for an hour or two. They soon lose their lustre, and undergo the changes noticed in heating zinc sulphate.

Compounds which lose their water of crystallization by simple contact with the air are said to *effloresce*. They are called *efflorescent*.

Some compounds if deprived of their water of crystallization will take it up again when allowed to lie in an atmosphere containing moisture. As the air always contains moisture, it is only necessary to expose such compounds to the air in order to notice the phenomenon. It is well shown by the compound calcium chloride,  $\text{CaCl}_2$ . This substance has a remarkable power of attracting water to itself and holding it in combination.

**EXPERIMENT 42.**—Expose a few pieces of calcium chloride to the air. Its surface will soon give evidence of the presence of moisture, and, after a time, the substance will dissolve in the water which is absorbed.

Substances which absorb water from the air are said to *deliquesce*. They are called *deliquescent*.

**Formation of Water and Proofs of its Composition.**—In order to determine the composition of water, as well as

that of any other compound, we must analyze it. We may simply determine what substances enter into its composition without determining the relative quantities of these substances. In this case we make what is called a *qualitative analysis*. If, however, we not only determine what substances are present, but also in what quantities they are present, we then make a *quantitative analysis*. Both qualitative and quantitative analyses are necessary to enable us to determine the composition of a substance.

The composition of a substance may also be determined by putting together its constituents and causing them to combine chemically. An operation of this kind is called a *synthesis*. A synthesis, then, is the opposite of an analysis. Just as we may make a qualitative or a quantitative analysis, so also we may make a *qualitative* or a *quantitative synthesis*.

These processes are well illustrated in the operations necessary to determine the composition of water. That water contains hydrogen and oxygen has already been shown in Experiment 3. It will now be well to repeat the experiment and see whether we can learn anything more regarding the composition of water than that it contains hydrogen and oxygen. In the first place, the question suggests itself; In what proportions, by weight and by volume, are the gases combined?

**EXPERIMENT 43.**—The tubes in the apparatus used in Experiment 3, or some other similar apparatus, should be marked by means of a file, or by etching, so that equal divisions can be recognized. Tubes thus divided so that the divisions indicate cubic centimetres are most convenient for the purpose. Let the gases formed by the action of the electric current, as in Experiment 3, rise in the graduated

tubes, and observe the volumes. It will be seen that when one tube is just full of gas, the other, if it be of the same size, will be only half full. On examining the gases the larger volume will be found to be hydrogen, and the smaller volume oxygen.

No matter how many times we may make this experiment, we shall always find that for every volume of oxygen we get two volumes of hydrogen. We already know the relative weights of equal volumes of the two gases, so that we can easily calculate the relative weights of the gases obtained from water by the action of the electric current. The ratio of the weights of equal volumes of hydrogen and oxygen is  $1 : 16$ . Therefore, if we have two volumes of hydrogen combined with one volume of oxygen, the ratio between the weights is  $2 : 16$  or  $1 : 8$ . Although we know from the above experiment that hydrogen and oxygen are obtained from water in the proportion of two volumes of the former to one of the latter, or of one part by weight of the former to eight parts by weight of the latter, we do not know from the experiment that this represents the actual composition of water. For it may be that other elements besides hydrogen and oxygen are contained in the water, and it may be that all the hydrogen and oxygen are not set free by the action of the electric current. We might determine whether either of these possibilities is true or not by decomposing a weighed quantity of water, and weighing the hydrogen and oxygen obtained from it. If we should find that the sum of the weights of hydrogen and oxygen is equal to the weight of the water decomposed, this fact would be evidence that only hydrogen and oxygen are contained in water, and that they are present in the proportions stated. The same thing can be satisfactorily proved

by effecting the synthesis of water. In the first place, we can show that water is formed when hydrogen burns in the air, and, knowing that burning is combining with oxygen, we are justified in concluding that water consists of hydrogen and oxygen.

**EXPERIMENT 44.**—Pass hydrogen from a generating-flask or a gasometer through a tube containing some substance that will absorb moisture, for all gases made in the ordinary way and collected over water are charged with moisture. We have seen in Experiment 42 that calcium chloride has the power to absorb moisture. It is extensively used in the laboratory for the purpose of drying gases, and it may be used in the present experiment. It should be in granulated form, not powdered. After passing the hydrogen through the calcium chloride, pass it through a tube ending in a narrow opening, and set fire to it. If now a *dry* vessel be held over the flame, drops of water will condense on its surface and run down. A convenient arrangement of the apparatus is shown in Fig. 19.

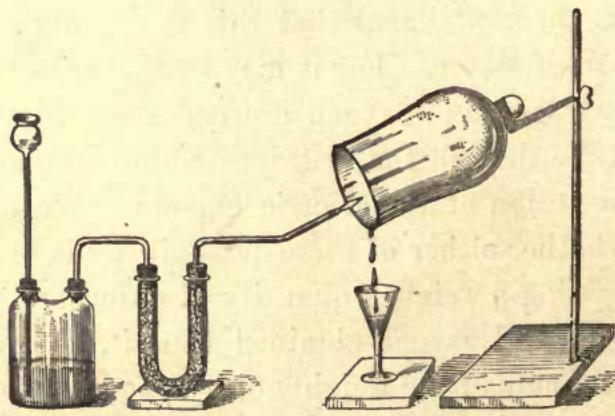


FIG. 19.

*A* is the calcium chloride tube. Before lighting the jet hold a glass plate in the escaping gas, and see whether

water is deposited on it. Light the jet *before* putting it under the bell jar, otherwise if hydrogen is allowed to escape into the vessel it will contain a mixture of air and hydrogen, and this mixture, as we shall soon see, is explosive.

We have thus effected the qualitative synthesis of water; how can we effect the quantitative synthesis?

If we mix hydrogen and oxygen together, and allow the mixture to stand unmolested, it remains unchanged. If, however, we should bring a spark or a flame in contact with the mixture, a violent explosion would occur, and a careful examination would show that the explosion is the result of the combination of the two gases. The noise is caused by the sudden great expansion of the gases occasioned by the development of heat. This expansion is instantly followed by a contraction.

**EXPERIMENT 45.**—Mix hydrogen and oxygen in the proportions of about 2 volumes of hydrogen to 1 volume of oxygen in a gasometer. Fill soap-bubbles, made as directed in Experiment 34, with this mixture and allow them to rise in the air. As they rise bring a lighted taper in contact with them, when a sharp explosion will occur. Great care must be taken to keep all flames away from the vicinity of the gasometer while the mixture is in it. This experiment may be conveniently performed by hanging up, about six to eight feet above the experiment-table, a good-sized tin funnel-shaped vessel with the mouth downward. Now place a gas jet or a small flame of any kind at the mouth of the vessel. If the soap-bubbles are allowed to rise below this apparatus they will come in contact with the flame and explode at once.\*

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\* The same apparatus may be used in experimenting with soap-bubbles filled with hydrogen.

This experiment simply shows that a mixture of hydrogen and oxygen explodes when brought in contact with a flame, and that the gases do not act upon each other at ordinary temperatures. In order to show that when the explosion occurs, water is formed, and in what proportions the gases combine, it is necessary to work in closed vessels which are so constructed as to enable us accurately to measure the volumes of the gases. The experiment is so important that, if possible, it had better be performed, at least by the teacher, before the class. The apparatus necessary is not expensive, and the manipulation not difficult. The vessel in which the gases are brought together and caused to combine is called a *eudiometer* (from *εὐδία*, calm air, and *μέτρον*, a measure). It is simply a tube graduated in millimetres and having two small platinum wires passed through it at the closed end, nearly meeting inside and ending in loops outside, as shown in Fig. 20. The eudiometer is filled with mercury, in-



FIG. 20.

verted in a mercury trough, and held in upright position by means of proper clamps. A quantity of pure hydrogen is now passed up into the tube and its volume accurately measured. About half this volume of oxygen is then introduced, and after the mixture has been allowed to stand for a few minutes, a spark is passed between the wires in the eudiometer by connecting the loops with the poles of a small Ruhmkorff coil or with a Leyden jar. Under these circumstances the explosion takes place noiselessly and with very little danger. If the interior of the tube was dry be-

fore the explosion, it will be seen to be moist afterwards, and a marked decrease in the volume of the gases is also observed. That water is the product of the action has been proved beyond any possibility of a doubt, over and over again. As the liquid water which is formed occupies an almost inappreciable volume as compared with the volume of the gases which combine, the decrease in volume represents the total volume of hydrogen and oxygen which have combined. Now, if the experiment be performed with the two gases in different proportions, it will be found that only when they are mixed in the proportion of two volumes of hydrogen and one volume of oxygen do they completely disappear in the explosion. If there is a larger proportion of hydrogen present, the excess is left over. If there is a larger proportion of oxygen present, the excess of oxygen is left over. We see, thus, that when hydrogen and oxygen combine to form water, they do so in the proportion of two volumes of hydrogen to one volume of oxygen. In order that the student may fully appreciate this experiment, it is desirable that he should at this point familiarize himself with the precautions necessary in measuring the volumes of gases, if he has not already done so.

**Measurement of the Volume of a Gas.**—The volume of a gas varies with the temperature and pressure. When the temperature of a gas is raised one degree Centigrade its volume is increased  $\frac{1}{273}$  part. If, therefore, the volume of a gas at  $0^{\circ}$  be  $V$ , at  $t^{\circ}$  its volume  $v$  will be

$$V + \frac{t}{273} \cdot V \quad \text{or} \quad v = V + \frac{t}{273} \cdot V.$$

This expression may also be written

$$v = V + 0.00366 t \cdot V \quad \text{or} \quad v = V(1 + 0.00366 t).$$

From this it follows that

$$V = \frac{v}{1 + 0.00366 t}.$$

It is customary to reduce the observed volume of a gas to the volume which it would have at  $0^\circ$ . The correction is made in accordance with the above expression. Thus, if we measure a volume of gas, and find it to be 250 cubic centimetres at  $15^\circ$ , and wish to find what its volume would be at  $0^\circ$ , we proceed as follows: In this case  $v$ , the observed volume, is 250 cc.;  $t$ , the temperature, is  $15^\circ$ . Substituting these values in the equation  $V = \frac{v}{1 + 0.00366 t}$ , we have

$$V = \frac{250}{1 + 0.00366 \cdot 15},$$

from which we get 236.99 as the value of  $V$ . But the volume of a gas varies also according to the pressure. If the pressure be doubled, the volume is decreased to one half; and if the pressure be decreased to one half, the volume is doubled, and so on. In other words, the volume of a gas varies inversely with the pressure. Increase the pressure two, three, or four times and the volume becomes one half, one third, or one fourth, and *vice versa*. If the gas has the volume  $V$  at the pressure  $P$  and at pressure  $p$  the volume  $v$ , these values bear to each other the relations expressed in the equation

$$PV = pv.$$

The pressure is usually stated in millimetres, and reference is to the height of a column of mercury which the pressure corresponds to. A gas contained in an open vessel, or in a vessel over mercury in water, in which the level of the liquid inside and outside the vessel is the same, is

under the pressure of the atmosphere. What that is we learn from the barometer. As this pressure varies, it is necessary to read the barometer whenever a gas is measured, and then to reduce the observed volume to certain conditions which are accepted as standard. If the gas is measured in a tube over mercury or water, and the level of the liquid inside the tube is higher than that outside, the gas is under diminished pressure, the amount of diminution depending on the height of the column of mercury or water in the tube. Thus, if the arrangement be as represented in Fig. 21 and the height of the mercury column above the level of the mercury in the trough be 100 millimetres, and the pressure of the atmosphere be 760 millimetres, then the gas in the tube is not under the full atmospheric pressure, for the atmospheric pressure exerted on the gas is supporting a column of mercury 100 millimetres high, and the pressure actually brought to bear on the gas corresponds to  $760 - 100 = 660$  mm. Suppose that in this case the volume of gas actually measured is 75 cc. Call this  $v$ . What would be the actual volume  $V$  of the gas under the standard pressure 760 mm. ? We have seen that

$$VP = vp.$$

Now  $P = 760$ ,  $v = 75$ , and  $p = 660$ . Therefore,  $760 V = 75 \times 660$ , or  $V = \frac{75 \times 660}{760} = 65.13$ .

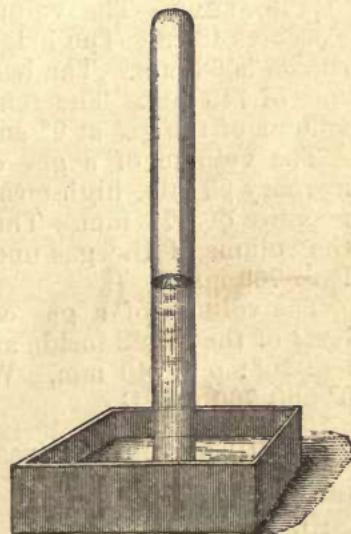


Fig. 21.

In all cases it is necessary to make a correction similar to this in dealing with the volumes of gases. The correction for temperature and that for pressure may be made in one operation, the formula being

$$V = \frac{vp}{760(1 + 0.00366t)},$$

in which  $V$  = the volume of the gas at  $0^\circ$  and 760 mm. pressure;  $v$  = the observed volume;  $t$  = the observed temperature;  $p$  = the pressure under which the gas is measured.

[PROBLEMS.—The volume of a gas contained in a eudiometer measures 42 cc. The height of the mercury column over which it stands is 68 mm. The barometer indicates an atmospheric pressure of 746 mm. The temperature is  $18^\circ\text{C}$ . What would be the volume of the gas at  $0^\circ$  and 760 mm. pressure ?

The volume of a gas contained in a vessel over a column of mercury 85 mm. high measures 24 cc. The barometer indicates a pressure of 774 mm. The temperature is  $19^\circ$ . What would be the volume of the gas under normal conditions, i.e.,  $t = 0^\circ$  and  $P = 760$  mm.?

The volume of a gas contained in a vessel over a liquid, the level of the liquid inside and outside being the same:  $v = 80$  cc.;  $t = 20^\circ$ ;  $p = 740$  mm. What is the value of  $V$  or the volume at  $0^\circ$  and 760 mm.?

It will be found hereafter that some of the most important ideas which have been introduced into chemistry with the view of explaining the regularities observed in the quantities of substances which act upon one another chemically have their origin in observations upon the conduct of gases. It is therefore highly desirable that the student should fully understand what is meant by the expression “the volume of a gas under standard conditions,” and it is recommended that he be given a few actual examples in which he shall make all the observations and calculations necessary.

The presence of water vapor in a gas also influences its

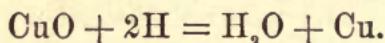
volume, and this must be taken into account in refined work. The student is referred to some larger book for details.

Let us now return to the problem of determining the composition of water by means of explosions in the eudiometer. It remains to be shown how to calculate the composition of water from the observations made.

**Calculation of the Results Obtained in Exploding Mixtures of Hydrogen and Oxygen.**—Having determined that whenever hydrogen and oxygen combine, they do so in the proportion 1 volume oxygen to 2 volumes hydrogen, and that when they combine, the volume of water formed measures so little as to amount to nothing in the measurements, we know that whenever a mixture of hydrogen and oxygen is exploded, no matter in what proportions they may be present, the volume of gas which disappears as such consisted of 2 volumes of hydrogen and 1 volume of oxygen, or, in other words, one third of the volume which disappears was oxygen and two thirds hydrogen. Take this example: A quantity of hydrogen corresponding to 60 cc. under standard conditions is introduced into a eudiometer; 40 cc. of oxygen are added. What contraction will there be on exploding the mixture? Plainly the 60 cc. of hydrogen will combine with 30 cc. of oxygen. The 90 cc. of gas will disappear, and the 10 cc. of oxygen will remain unchanged. From a total volume of 100 cc., therefore, we get a contraction to 10 cc. One third of the contraction represents the oxygen and two thirds the hydrogen.

**Synthesis of Water by Passing Hydrogen over Heated Oxides.**—The synthesis of water may be effected by passing hydrogen over a compound containing oxygen and heated to a sufficiently high temperature. A convenient sub-

stance for this purpose is the compound of copper and oxygen known as copper oxide or black oxide of copper. It contains its elements in the proportions represented in the formula CuO, the combining weight of copper being 63. When hydrogen is passed over this compound at ordinary temperatures no action takes place. If, however, the temperature be raised to low redness the hydrogen combines with the oxygen, forming water, and the copper is left behind as such. The reaction is represented thus:



**EXPERIMENT 46.**—Arrange an apparatus as shown in Fig. 22.

*A* is a Wolff's flask for generating hydrogen. To remove impurities the gas is passed through a solution of

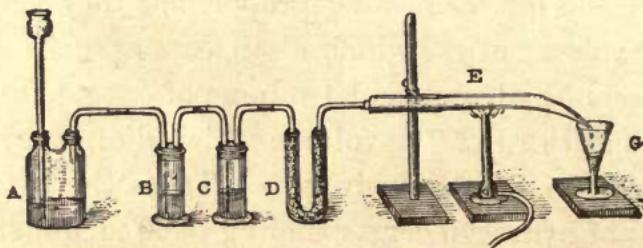


FIG. 22.

potassium permanganate contained in the wash cylinder *B*. The cylinder *C* contains concentrated sulphuric acid, and the U-shaped tube *D* contains granulated calcium chloride, both of them serving to remove moisture from the gas. The pure dry hydrogen is now passed through the hard glass tube *E*, which contains a layer of copper oxide. After the apparatus is filled with hydrogen the gas jet is lighted and the copper oxide heated to low redness. Soon moisture will be seen in the end of the tube and drops of water will collect in the vessel *G*.

In this case the loss in weight of the copper oxide repre-

sents oxygen. If, therefore, we should weigh the copper oxide before the experiment, and afterward the copper, and should also collect and weigh the water formed, we could from the figures obtained easily calculate the relative weight of oxygen contained in the water. The water can easily be collected by passing it into a tube filled with calcium chloride. If the tube is weighed before the experiment and after it, the gain in weight will represent the weight of the water collected. All these weighings can be made without difficulty on a chemical balance such as is found in every chemical laboratory. Where time will permit it will be well for each student to go through with this experiment. A few experiments of this kind will serve to impress upon the mind the reality of the quantitative relations about which he is constantly hearing. If it is performed a small hard glass tube from 12 to 15 centimetres (5 to 6 inches) long and about 1 centimetre (or half an inch) internal diameter should be used in place of the tube *E* in the qualitative experiment above described. The tube is drawn out at one end and a small plug of asbestos put in the small end. Connection with the weighed calcium chloride tube is made at this end. The tube is first dried thoroughly and weighed. Then a few grams of coarsely granulated copper oxide are introduced into it. After the experiment the tube and the copper are weighed again. The calcium chloride should of course be weighed before and after the experiment. The results are calculated thus:

Let  $x = \text{weight of tube} + \text{copper oxide before the experiment};$   
 $y = \text{weight of tube} + \text{copper after the experiment}.$

Then  $x-y$  = weight of oxygen taken from the copper oxide.

Let  $a$  = weight of calcium chloride tube before;  
 $b$  = " " " " " after;

Then  $b-a$  = weight of water formed.

If the experiment is carefully performed, it will be found that the ratio  $\frac{x-y}{b-a}$  is very nearly  $\frac{8}{9}$ .

**Oxidation and Reduction.**—Any substance which like hydrogen has the power to abstract oxygen from compounds containing it is called a *reducing agent*. The proc-

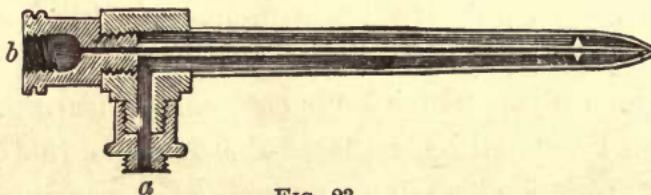


FIG. 23.

ess of abstracting oxygen from a compound is called *reduction*. *Reduction* and *oxidation* are therefore complementary processes. We shall hereafter become acquainted with a number of important and interesting reducing processes.

**Applications of the Heat Evolved by the Combination of Hydrogen and Oxygen.**—The heat evolved when hydrogen combines with oxygen is very great, and it is utilized for various purposes. To burn hydrogen in the air is, as we have seen, a simple matter, but to burn it in oxygen requires a special apparatus to prevent the mixing of the gases before they reach the end of the tube where the combustion takes place. The *oxyhydrogen blow-pipe* answers this purpose. It is simply a tube with a smaller tube passing through it, as shown in Figure 23.

The hydrogen is admitted through *a* and the oxygen through *b*. It will be seen that they come together only at the end of the tube. The hydrogen is first passed through and lighted; then the oxygen is passed through slowly, the pressure being increased until the flame appears thin and straight. It gives very little light, but is intensely hot.

**EXPERIMENT 47.**—Hold in the flame of the oxyhydrogen blow-pipe successively a piece of iron wire, a piece of a steel watch-spring, a piece of copper wire, a piece of zinc, a piece of platinum wire.

The metal platinum is used for many purposes, particularly for chemical operations. The vessels are made from molten platinum, and the metal is melted by means of the oxyhydrogen blow-pipe.

When the flame is allowed to play upon some substance which it cannot melt nor burn up, the substance becomes heated so high that it gives off an intense light. The substance commonly used is quicklime. Hence the light is often called the lime light. It is also known as the Drummond light.

**EXPERIMENT 48.**—Cut a piece of lime of convenient size and shape, say an inch long by three quarters of an inch wide, and the same thickness. Fix it in position so that the flame of the oxyhydrogen blow-pipe will play upon it. The light is very bright, but by no means as intense as the electric light.

**Properties of Water.**—Though, as we know, water is widely distributed over the earth, we never find perfectly pure water. All natural waters contain foreign substances in solution. These foreign substances are taken up from the air, or from the soil. In order to get pure water, it is distilled. Distillation consists in boiling the water, and

then condensing the vapor by passing it through a tube which is kept cool by surrounding it with cold water. A simple apparatus for the purpose is that illustrated in Fig. 24.

The water to be distilled is placed in the flask *A*. The flask is connected by means of a bent glass tube *B* with the long tube *CC*. This in turn is surrounded by the larger tube or jacket *D*. The side tube *E* is connected

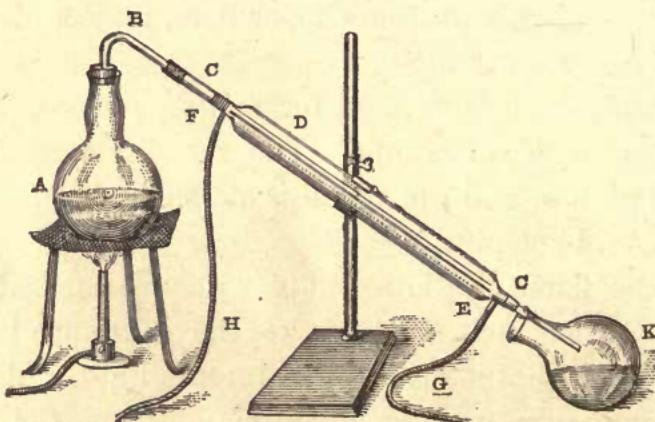


FIG. 24.

with a faucet by means of the rubber tube *G*. The water is allowed to flow slowly into the jacket and out at *F*, whence it passes through the rubber tube *H* to the sink. When the water in *A* is boiled, the vapor passes into the tube *CC*. Here it is cooled down, and takes the form of liquid, which runs down and collects in the flask *K*, which is called the receiver.

**EXPERIMENT 49.**—Dissolve some copper sulphate, or other colored substance, in a litre of water, and distil the water.

By means of distillation most substances held in solution in water can be gotten rid of. Substances which are volatile, however, will of course pass over with the water vapor.

The purest water found in nature is rain water, particularly that which falls after it has rained for some time. That which first falls always contains impurities from the air. As soon as the rain water comes in contact with the earth, and begins its course towards the ocean, it begins to take up various substances, according to the character of the soil with which it comes in contact. Mountain streams which flow over rocky beds, particularly over beds of sandstone, which is very insoluble, contain exceptionally pure water. Streams which flow over limestone dissolve some of the stone, and the water becomes "hard." The many varieties of mineral springs have their origin in the presence in the earth of certain substances which are soluble in water. Common salt occurs in large quantities in different parts of the earth. As it is easily soluble in water, many streams contain it; and as all the streams find their way into the ocean, we see one reason why the water of the ocean should be salt. As streams approach the habitations of man they are subjected to a serious cause of contamination. The drainage from the neighborhood of human dwellings is very apt to find its way into a near stream. This condition of things is most strikingly illustrated by the case of a large town situated on the banks of a river. It frequently happens that the water of the river is used for drinking purposes, and it also frequently happens that the water is contaminated by drainage. Water when once contaminated by drainage tends to become pure again by contact with the air. If it is to be used for drinking purposes, however, it is not well to rely too much upon this process of purification.

Pure water is tasteless and inodorous. In thin layers it is colorless, but in thick layers it is blue. This has

been shown in the laboratory by filling a long tube with distilled water. When looked through it appears blue. The beautiful blue color of the water of some lakes is the natural color of pure water.

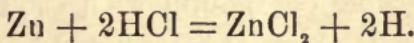
On cooling, water contracts until it reaches the temperature of  $4^{\circ}$ . At this point it has its maximum density. When cooled below  $4^{\circ}$  it expands, and the specific gravity of ice is somewhat less than that of water. Hence ice floats on water.

**Uses of Water in Chemistry.**—Water is the best solvent. A greater number of substances dissolve in it than in any other liquid. Chemical operations are very frequently carried on in solution. That is to say, the substances which are to act chemically upon one another are first brought into solution. The object of this is to get the substances into as close contact as possible. If we rub two solids together, the particles remain separated by sensible distances, no matter how finely the mixture may be powdered. If, however, the substances be dissolved, and the solutions poured together, the particles of the liquid move so freely among one another that they come in intimate contact, thus facilitating chemical action. In some cases substances which do not act upon one another at all when brought together in dry condition act readily when brought together in solution.

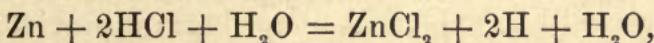
**Solution.**—In a solution the particles of the solid dissolved are in some way attracted and held in combination by the particles of the liquid. There is a definite limit to the amount of any substance which can thus be held in solution at a given temperature. The substance dissolved is distributed uniformly through the solution, no matter how dilute or how concentrated the solution may be, provided

it has stood long enough, or has been thoroughly mixed by stirring.

In representing by an equation a reaction which takes place between substances in solution, it is not customary to take account of the water, which mainly plays the part of a solvent. We have already had an illustration of this in the case of hydrochloric acid and zinc. What we call hydrochloric acid in the laboratory is a solution of the gas, HCl, in water. When this solution is used, however, it is the hydrochloric acid itself, *i.e.*, the compound HCl, which acts, while the rôle played by the water is secondary. Therefore the water does not appear in the equation:



We might indeed represent the action thus:



but this would only complicate the matter without in any way helping us.

**Ozone.**—When electric sparks are passed for a time through oxygen it undergoes a remarkable change. It acquires a strong odor, and is much more active than under ordinary circumstances. The odor of the gas is observed in the neighborhood of an electric machine in action, and is said to be noticed during thunder showers. The substance which has the odor is ozone. It is formed in a number of chemical reactions, as when phosphorus acts on the air in the presence of water. By cold and pressure it has been obtained in the form of a dark-blue liquid.

When a certain volume of oxygen is converted into ozone the volume of gas is decreased from three to two.

By heating ozone above 300° it is converted into ordinary oxygen, and its volume is increased from two to three.

It is clear that the element oxygen can be converted into something else without the addition of anything to it. This might lead us to conclude that it is not an element. But the substance formed from it has exactly the same weight and can be changed back again to oxygen without anything being added to it. It follows that the change must take place within the oxygen itself. The commonly accepted explanation of the relation between oxygen and ozone will be given later. (See Chapter XI., Molecular Weights.)

Ozone is present in small quantity in the air.

**Hydrogen Dioxide,  $H_2O_2$ .**—Besides water, hydrogen and oxygen form a second compound with each other. This is hydrogen dioxide,  $H_2O_2$ .\* It is prepared by treating barium dioxide,  $BaO_2$ , with sulphuric acid. The reaction which takes place will be explained under barium dioxide.

Hydrogen dioxide is a liquid which breaks up readily into water and oxygen. The ease with which it gives up oxygen makes it a good oxidizing agent. It is now manufactured on the large scale.

**Summary.**—We have thus learned that (1) water can be decomposed into hydrogen and oxygen by means of an electric current; (2) the gases are obtained in the proportion of eight parts by weight of oxygen to one part by weight of hydrogen, or one volume of oxygen to two volumes of hydrogen; (3) when hydrogen is burned water is formed; (4) when hydrogen and oxygen are mixed together they do not combine under ordinary circumstances; (5) when a spark or flame is brought in contact with the mixture violent action takes place accompanied by explosion; (6) the

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\* The reason for writing this formula  $H_2O_2$  and not HO will be seen after studying Chapter XI.

action is occasioned by the chemical combination of the two gases; (7) they combine in the same proportions as those in which they are obtained from water by the action of the electric current; (8) water can be made by passing hydrogen over heated copper oxide; (9) by weighing the copper oxide before and after the experiment, and determining the weight of the water formed, the proportion of water which consists of oxygen is found to be eight ninths.

All these facts taken together prove that the composition of water is what it has been stated to be. Now, using the accepted combining weights of hydrogen and oxygen, viz., 1 and 16,—the simplest formula which expresses the composition of water is  $H_2O$ . This expresses the fact that water is composed of 2 parts by weight of hydrogen and 16 parts by weight of oxygen, or 1 part of the former to 8 of the latter. It will be noticed that the formula also indicates the volumes of the gases which enter into combination with each other. Two volumes of hydrogen are combined with one of oxygen, and two combining weights of hydrogen are combined with one combining weight of oxygen,  $H_2O$ . This is, of course, connected with the remarkable fact, to which attention has already been called (see *ante*, p. 68), that the combining weights of hydrogen and oxygen bear the same relation to each other that the absolute weights of equal volumes of the gases do.

**Comparison of Hydrogen and Oxygen.**—Hydrogen and oxygen are different kinds of matter, just as heat and electricity are different kinds of energy. Heat can be converted into electricity, and electricity into heat, but one element cannot by any means known to us be converted into another. They are apparently entirely independent of each other. The question will therefore suggest itself, whether,

in spite of their apparent independence, there is not some relation between the different elements which reveals itself by similarity in properties? It will be found that the elements can be divided into groups or families according to their properties. There are some elements, for example, which in their chemical conduct resemble oxygen markedly. These elements make up the *oxygen family*. So far as hydrogen is concerned, however, it stands by itself. There is no other element which conducts itself like it. If we compare it with oxygen, we find very few facts which indicate any analogy between the two elements. In their physical properties they are, to be sure, similar. Both are transparent, colorless, inodorous gases. On the other hand, oxygen combines readily with a large number of substances with which hydrogen does not combine. Oxygen, as we have seen, combines easily with carbon, sulphur, phosphorus, and iron. It is a difficult matter to get any of these elements to combine directly with hydrogen. Further than this, substances which combine readily with hydrogen do not combine readily with oxygen. The two elements exhibit opposite chemical properties. What one can do, the other cannot do. This oppositeness of properties is favorable to combination; for not only do hydrogen and oxygen, with their opposite properties, combine with great ease under the proper conditions, but, as we shall see later, it is a general rule that elements of like properties do not readily combine with one another, while elements of unlike properties do readily combine with one another.

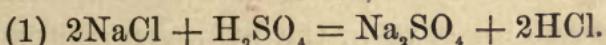
We shall next take up the study of a third element, which is widely distributed in nature, which in some respects resembles both hydrogen and oxygen, and in some respects differs from each. This is the element chlorine.

## CHAPTER V.

### CHLORINE AND ITS COMPOUNDS WITH HYDROGEN AND OXYGEN.

**Occurrence.**—Chlorine, though widely distributed in nature, does not occur in very large quantity as compared with oxygen and hydrogen. It is found chiefly in combination with the element sodium as common salt, or sodium chloride, which has the composition represented by the formula NaCl. It is also found in combination with other elements, as potassium, magnesium, etc. In comparatively small quantity it occurs in combination with silver, forming one of the most valuable silver ores. All the chlorine with which we have to deal is made from common salt.

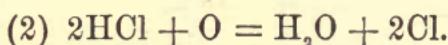
**Preparation.**—It is not practicable to decompose sodium chloride directly into its elements. In order to get the chlorine out of the compound in the free state, it is necessary, first, to get it in combination with hydrogen in the form of hydrochloric acid, HCl. This is very easily accomplished by treating salt with ordinary sulphuric acid. When the two are brought together a change takes place, which will be studied more in detail farther on. The reaction is represented thus :



As will be seen, the sodium of the sodium chloride and the hydrogen of the hydrochloric acid exchange places,

a kind of action which is quite common. This particular reaction is of very great importance in the arts, as it is the first stage in the preparation of common "soda" or sodium carbonate, and of chlorine.

Now, if hydrochloric acid be brought in contact with a substance which gives up oxygen easily, the hydrogen will unite with the oxygen to form water, and the chlorine will be set free. The reaction is expressed thus:

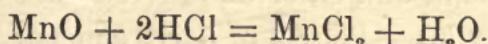


[PROBLEM.—How much sulphuric acid will it require to set free enough hydrochloric acid to make 25 grams of chlorine?]

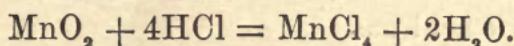
As we have an unlimited supply of oxygen in the air, it would be advantageous could we effect the decomposition of hydrochloric acid by means of the element in the free state. On the large scale this is now accomplished. Deacon's process for manufacturing chlorine consists in passing air and hydrochloric acid together through a heated tube containing clay balls saturated with copper sulphate. Exactly why the oxidation takes place under these circumstances is not known. The essential feature of the reaction is nevertheless the oxidation of the hydrochloric acid, as represented in equation (2).

For the preparation of chlorine in the laboratory it is most convenient to bring hydrochloric acid in contact with manganese dioxide,  $\text{MnO}_2$ , a substance which we have already had to deal with for the purpose of preparing oxygen. The action which takes place is explained thus: In the first place, when hydrochloric acid acts upon some compounds containing oxygen, the hydrogen and oxygen combine, and the element which was in combination with oxygen combines with chlorine. Thus, when the compound

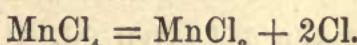
MnO is treated with hydrochloric acid, this reaction takes place.



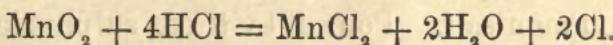
So, also, when manganese dioxide is treated with hydrochloric acid, the oxygen is probably first replaced by chlorine, as represented in the equation



But the compound  $\text{MnCl}_4$  gives up half of its chlorine when heated:



So that the action of hydrochloric acid on manganese dioxide is represented as follows:



[PROBLEM.—How much manganese dioxide would be required to liberate 50 grams of chlorine? The combining weight of manganese is 55.]

Instead of first making the hydrochloric acid from salt and then treating the hydrochloric acid with manganese dioxide, it is really best to mix together the manganese dioxide and common salt and pour upon the mixture the necessary quantity of sulphuric acid. For practical purposes mix 5 parts of coarsely granulated manganese dioxide and 5 parts of coarsely granulated common salt. Make a mixture of 12 parts of concentrated sulphuric acid and 6 parts of water.\* Let this mixture cool down thoroughly, and then pour it upon the mixture of salt and manganese dioxide. Gently heat, and a regular current of chlorine will be given off. This is by far the best way to make chlorine in the laboratory.

In this case the manganese dioxide and sulphuric acid give off oxygen, and the common salt and sulphuric acid

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\* See precautions necessary noted on p. 64.

give off hydrochloric acid. The oxygen then oxidizes the hydrochloric acid, and chlorine is given off.

**EXPERIMENT 50.**—Pour 2 or 3 cc. concentrated sulphuric acid on a gram or two of common salt in a test-tube. A gas will be given off which forms dense white fumes in the air and has a sharp, penetrating taste and smell. This is hydrochloric acid gas.

**EXPERIMENT 51.**—Pour 2 or 3 cc. concentrated sulphuric acid on a few grams of manganese dioxide in a test-tube. Heat, and examine the gas given off. Convince yourself that it is oxygen.

**EXPERIMENT 52.**—Mix 2 grams manganese dioxide and 2 grams common salt. Pour 4 to 5 cc. sulphuric acid on the mixture in a test-tube. This experiment should be performed under a hood in which the draught is good, as the gas which is given off is not only very disagreeable, but very irritating to the respiratory organs. Notice the color and odor of the gas. [Does it support combustion? Does it burn?]

**Properties.**—Chlorine is a greenish-yellow gas. It has a disagreeable smell, and acts upon the passages of the throat and nose, causing irritation and inflammation. The effect is much like that of “a cold in the head.” Inhaled in concentrated form, *i.e.*, not diluted with a great deal of air, it would cause death. It is much heavier than air, its specific gravity being 2.45. A litre of chlorine gas, under standard conditions, weighs 3.167 grams. It is soluble in water and acts upon mercury, and therefore cannot be collected by displacement of either of these liquids. The most convenient way to collect it is by displacement of air. The apparatus for the purpose is arranged as shown in Fig. 25. The delivery-tube should extend to the bottom of the col-

lecting vessel. This vessel should be dry, and its mouth covered with a piece of paper to prevent currents of air from carrying away the chlorine. As the gas collects in the vessel the experimenter can judge of the quantity present by the color.

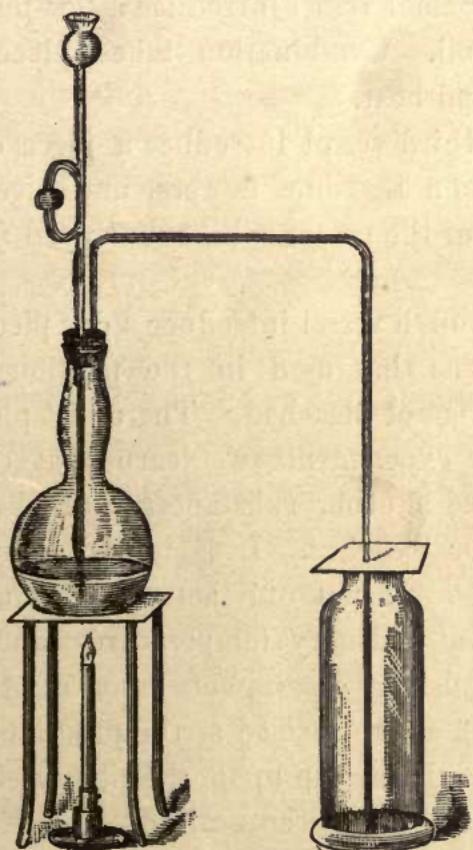


FIG. 25.

**EXPERIMENT 53.**—Collect six or eight dry cylinders or bottles full of chlorine. Make the gas from about 100 grams of manganese dioxide, using the other substances in the proportions already stated.

(1) Introduce into one of the vessels containing chlorine a little finely powdered antimony. The two elements com-

bine at once with evolution of light. The product is antimony trichloride,  $SbCl_3$ .

[In what respects does this experiment resemble the one in which iron was burned in oxygen? In what respects do the two differ?]

(2) Into a second vessel introduce a few pieces of heated thin copper foil. Combination takes place with evolution of light and heat.

(3) Into a third vessel introduce a piece of paper with some writing on it, some flowers, and pieces of colored calico. Most of the colors will be destroyed *if the substances are moist.*

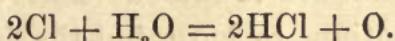
(4) Into a fourth vessel introduce a dry piece of the same colored calico as that used in the previous experiment. The dry piece is not bleached. The moist piece is.

From these experiments we learn that chlorine combines readily with other substances, and also that it destroys colors or bleaches. It is indeed one of the most active elements. It not only acts directly upon many of the elements at ordinary temperatures, and decomposes many compounds, but it also acts upon most organic substances, or such as are formed as the products of animal or vegetable life. Its action upon the tissues of the respiratory organs has already been noticed.

**EXPERIMENT 54.**—Cut a piece of filter-paper about an inch wide and six to eight inches long. Pour on this some ordinary oil of turpentine previously warmed slightly. Introduce this into the sixth vessel of chlorine. A flash of flame is noticed and a dense cloud of black smoke is formed. The action here is due to the great affinity of chlorine for hydrogen. Oil of turpentine consists of carbon and hydrogen. The main action of the chlorine con-

sists in extracting the hydrogen and leaving the carbon. The experiment is interesting chiefly in so far as it illustrates the general tendency of chlorine to act upon vegetable substances.

It was noticed that when moisture is present chlorine bleaches, while when it is not present bleaching does not take place. The reason of these facts is interesting. Chlorine acts directly upon some dye-stuffs, converting them into colorless substances. In other cases it has been shown that the destruction of the color is due to oxygen, which is set free from water by the action of chlorine. In the direct sunlight chlorine decomposes water according to this equation:



**EXPERIMENT 55.**—Seal the end of a glass tube about a metre (or about a yard) long and about 12 mm. ( $\frac{1}{2}$  inch) internal diameter. Fill this with a strong solution of chlorine in water. Invert it, as shown in Fig. 26, in a shallow vessel containing some of the same solution of chlorine in water. Place the tube in direct sunlight. Gradually bubbles of gas will be seen to rise and collect in the upper end, and the color of the solution, which is at first greenish-yellow, like that of chlorine, disappears. The gas can be shown to be oxygen.

In bleaching, this decomposition of water takes place in direct contact with the colored materials, and the oxygen, the instant it is set free, is more active than free oxygen is. It is this oxygen which is being set free which acts upon the colored substances and converts them into colorless substances.



FIG. 26.

**Chlorine Hydrate.**—When chlorine gas is passed into water cooled down almost to the freezing point, crystals appear in the vessel. These consist of chlorine and water and are known as *chlorine hydrate*. Its composition is represented by the formula  $\text{Cl} + 5\text{H}_2\text{O}$ . The crystals are very unstable, breaking up at the ordinary temperature into chlorine gas and water.

The ease with which chlorine decomposes water and vegetable substances containing hydrogen shows that it has a strong affinity for hydrogen. Just as hydrogen burns in oxygen, it also burns in chlorine.

**EXPERIMENT 56.**—Light a jet of hydrogen in the air and carefully introduce it into a vessel containing chlorine. It will continue to burn, but the flame will not appear the same. A gas will be given off which forms clouds in the air. This gas has a sharp, penetrating taste and smell.

The burning of hydrogen in air or oxygen is simply the act of combination of hydrogen and oxygen, the product being water in the state of vapor, and therefore invisible. When hydrogen burns in chlorine the action consists in the union of the two gases, the product being hydrochloric acid,  $\text{HCl}$ , which forms the clouds in the air. In both cases the action is accompanied by an evolution of heat and light.

Just as the compounds of oxygen with other elements are called oxides, so the compounds of chlorine with other elements are called *chlorides*. We distinguish between the different chlorides in the same way that we distinguish between the different oxides (see p. 57).

**Hydrochloric Acid.**—The only compound which chlorine and hydrogen form with each other is hydrochloric

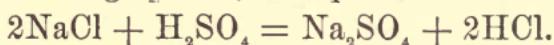
acid. It has already been shown that hydrogen burns in chlorine and that hydrochloric acid is formed. The two gases may be mixed together and allowed to stand together indefinitely in the dark and no action will take place. If, however, the mixture be put in diffused sunlight, gradual combination takes place; and if the direct light of the sun be allowed to shine for an instant on the mixture, explosion occurs, and this is the sign of the combination of the two gases. The same sudden combination is effected by applying a flame or spark to the mixture, or by illuminating it instantaneously with the light from a piece of burning magnesium or electric light.

[What difference is there between the combination of hydrogen and oxygen and of hydrogen and chlorine?]

The way in which the sunlight and other bright lights act upon the mixture of hydrogen and chlorine to cause them to combine is not understood; but the fact that sunlight does have a marked influence upon some kinds of chemical action is well known. One other illustration of this influence has already been before us, that of the decomposition of water by chlorine. This action does not take place in the dark. The sunlight is essential. The art of photography is based upon the influence of light in causing chemical changes. The light from the object photographed is allowed to act in the camera on a plate, upon the surface of which is a substance which is changed chemically by light. It should be specially noted that the cause of the chemical changes in these cases is not the heat but the light. If the substances are heated to the same temperature in the dark, the changes do not take place.

**Preparation.**—To prepare hydrochloric acid, common salt or sodium chloride, NaCl, is treated with sulphuric

acid (see Experiment 50, p. 97). As has already been explained, the hydrogen of the sulphuric acid and the sodium of the salt exchange places, as represented in the equation



The products are sodium sulphate and hydrochloric acid. The hydrochloric acid is given off as a gas, and the sodium sulphate remains behind in the flask.

**Properties.**—Hydrochloric acid is a colorless transparent gas. It has a sharp penetrating taste and smell. If inhaled into the lungs it produces suffocation. It dissolves in water very readily. At ordinary temperatures one volume of water will dissolve 450 times its own volume of the gas. The solution is the liquid known in the laboratory as hydrochloric acid.

[PROBLEM.—A litre of hydrochloric acid gas weighs 1.6283 grams at 0°. At 0° one volume of water will absorb 500 times its own volume of the gas. How much will a litre of water increase in weight at 0° by taking up all the hydrochloric acid it can?]

So strong is the attraction of hydrochloric acid for water that it condenses moisture from the air; hence, although the gas itself is quite colorless and transparent, when it comes in contact with the air dense white clouds are formed, which are not formed if it is kept from contact with the air.—Hydrochloric acid does not burn and does not support combustion. This is equivalent to saying that it does not combine with oxygen under ordinary circumstances, and that substances which combine with the oxygen of the air do not combine with hydrochloric acid.

[What evidence have we had that, under some circumstances, oxygen does act on hydrochloric acid? What are the circumstances? What are the products?]

Commercial hydrochloric acid is a yellowish liquid, the color being due to the presence of impurities. The solution is obtained in the factories in which “soda,” or sodium

carbonate is made. This is an extremely important substance in the arts. It does not occur in nature, but is manufactured from common salt. In the process most commonly used the salt is first converted into sodium sulphate by treating it with sulphuric acid. Hydrochloric acid is necessarily given off. When the factories were first established in England, the gas was allowed to escape as a waste product, but the effects produced by it upon the vegetation of the surrounding country were so destructive that a law was passed prohibiting the manufacturers from allowing the gas to escape. It is now collected by passing it through water. Thus enormous quantities of the solution are produced, but its uses are numerous and it always commands a price.

Pure hydrochloric acid is a solution of the pure gas in pure water. It is colorless, and when concentrated it gives off fumes when exposed to the air. The solution when heated gives off a large part of the gas contained in it, and by boiling it can all be evaporated.

**EXPERIMENT 57.**—Arrange an apparatus as shown in Fig. 27.

Weigh out 5 parts common salt, 5 parts concentrated sulphuric acid, and 1 part water. Mix the acid and water, taking the usual precautions ; let the mixture cool down to the ordinary temperature ; and then pour it on the salt in the flask. For the purposes of the experiment take about 100 grams of salt. Now heat the flask gently, and the gas will be regularly evolved. Conduct it at first through water contained in the three Wolff's bottles until what passes over is all absorbed in the first Wolff's bottle. The reason why gas at first bubbles through all the bottles is, that the apparatus is full of air, which is first driven out. When the air has been

displaced, the gas is all absorbed as soon as it comes in contact with the water.—After the gas has passed for ten to fifteen minutes, disconnect at *A*. Notice the fumes. These become denser by blowing the breath on them, as this increases the moisture in the vicinity.—Apply a lighted match to the end of the tube. The gas does not burn.—Collect some of the gas in a dry cylinder by displacement of air, as in the case of chlorine. The specific gravity of the gas being 1.26, the vessel must of course be placed with the mouth up-

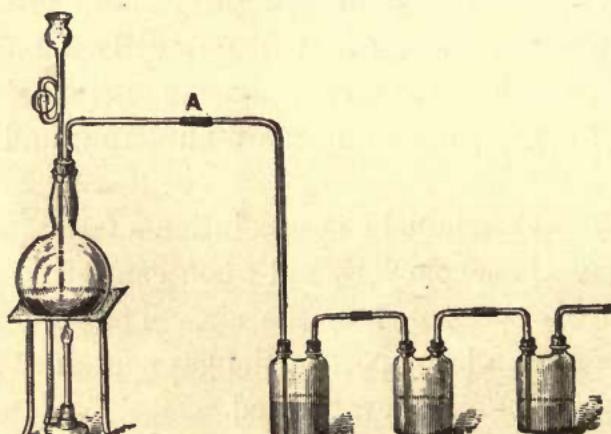
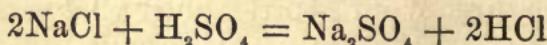


FIG. 27.

ward. That the gas is colorless and transparent is shown by the appearance of the generating flask, which is filled with the gas. Insert a burning stick or candle in the cylinder filled with the gas. It is extinguished.—Reconnect the generating-flask with the series of bottles containing water, and let the process continue until no more gas comes over. The reaction represented in the equation

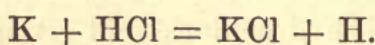


is now complete. After the flask has cooled down, pour water on the contents; and when the substance is dissolved

filter it and evaporate to such a concentration that, on cooling, the sodium sulphate is deposited. Pour off the liquid and dry the solid substance by placing it upon folds of filter-paper. Compare the substance with the common salt which you put in the flask before the experiment. What proofs have you that the two substances are not the same?—Heat a small piece of each in a dry tube closed at one end. What differences do you notice?—Treat a small piece of each in a test-tube with sulphuric acid. What difference do you notice?—If in the experiment we should recover all the sodium sulphate formed, how much would we have?—Put about 50 cc. of the liquid from the first Wolff's bottle in a porcelain evaporating-dish. Heat over a small flame just to boiling. Is hydrochloric acid given off? Can all the liquid be driven off by boiling?—Try the action of the solution on some iron filings. Is hydrogen given off?—Add some to a little granulated zinc in a test-tube. Is hydrogen given off?—Add a little to some manganese dioxide in a test-tube. Is chlorine given off?—Add ten or twelve drops of the acid to 2 to 3 cc. water in a test-tube. Taste the dilute solution. It has what is called a *sour* or *acid taste*, the two terms being practically synonymous.—Add a drop or two of a solution of *blue* litmus, or put into it a piece of paper colored *blue* with litmus. The color is changed to *red*. Litmus is a vegetable color prepared for use as a dye. Other vegetable colors are changed by hydrochloric acid.—Steep a few leaves of red cabbage in water. Add a few drops of the solution thus obtained to dilute hydrochloric acid. Is there any change in color?—The color will be restored in each case by adding a few drops of a solution of caustic soda.—In what experiment has caustic soda been obtained? What relation does it bear

to water?—To the dilute solution of hydrochloric acid add drop by drop a dilute solution of caustic soda. Is the acid taste destroyed?

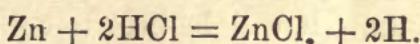
**Analysis of Hydrochloric Acid.**—The determination of the composition of hydrochloric acid is not as easily made as that of water. That it consists of hydrogen and chlorine is shown by the fact that it is formed by direct combination of these elements. To determine the relative weights and volumes of the gases which enter into combination, we may proceed thus: Enclose a suitable quantity of the gas in a tube. Introduce a small piece of the metal potassium. Decomposition will take place as represented in the equation



The gas left over is hydrogen. On measuring its volume it will be found to be just half that of the hydrochloric acid decomposed. The weight of the hydrogen obtained will be found to bear to the weight of the hydrochloric acid the proportion 1 : 36.5. In other words, in 36.5 parts of hydrochloric acid there are 35.5 parts of chlorine and 1 part of hydrogen. In 1 volume of the gas there is  $\frac{1}{2}$  volume of hydrogen. By mixing equal volumes of hydrogen and chlorine and causing them to combine it has been found that 1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrochloric acid. The specific gravity of the relative weights of equal volumes of hydrogen and chlorine are,—hydrogen, 0.0691; chlorine, 2.45. These figures bear to each other the same relation as the combining weights of the elements, viz., 1 : 35.5. [What fact of the same kind was noticed in comparing the specific gravities of hydrogen and oxygen?] Regarding

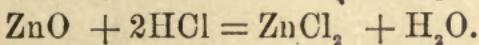
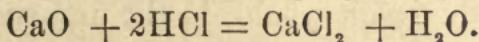
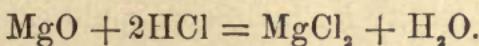
the chemical conduct of hydrochloric acid, we have learned from the experiments already performed:

1. That it gives up its hydrogen when brought in contact with certain substances like iron, zinc, etc., which belong to the class called metals; and that it takes up the metals in place of the hydrogen. Thus zinc and hydrochloric acid give zinc chloride and hydrogen:



2. That in contact with substances which give off oxygen, or with oxygen itself under certain circumstances, it gives up its chlorine, while the hydrogen combines with oxygen to form water.

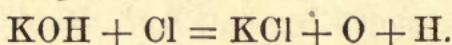
We shall learn hereafter that when it acts upon the compounds of the metals with oxygen or the so-called metallic oxides like magnesia or magnesium oxide,  $\text{MgO}$ ; lime or calcium oxide,  $\text{CaO}$ ; zinc oxide,  $\text{ZnO}$ , etc.,—compounds which do not easily give up oxygen,—the hydrogen of the acid combines with the oxygen of the oxide to form water, while the metals combine with the chlorine:



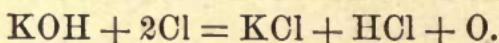
It will be noticed that when hydrochloric acid acts upon zinc oxide zinc chloride is formed. But this is the product obtained when hydrochloric acid acts upon the metal zinc. The metals calcium and magnesium act towards hydrochloric acid the same as zinc. Plainly the cause of these reactions is the strong attraction of chlorine for the metals.

**Compounds of Chlorine with Oxygen and with Hydrogen and Oxygen.**—As we have seen, chlorine combines very readily with hydrogen, and hydrogen with oxygen, and the products are stable compounds. On the other hand, chlorine cannot be made to combine directly with oxygen. By indirect processes they can be combined, but the compounds undergo decomposition easily, yielding back the chlorine and oxygen contained in them. Before considering these compounds it will be best to consider, as far as may be necessary, the compounds of chlorine, hydrogen, and oxygen which are more easily made, and from which the oxides are made.

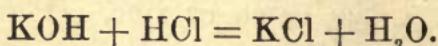
**Compounds of Chlorine with Hydrogen and Oxygen.**—One of the principal reactions made use of for the preparation of compounds of chlorine, oxygen, and hydrogen consists in treating caustic potash, or potassium hydroxide, KOH, with chlorine. We have learned that chlorine has a strong affinity for metals. Now, if chlorine is brought together with potassium hydroxide we would expect it to combine with the potassium thus:



But its strong affinity for hydrogen would cause the two to unite, so that the result would, in the first stage, be represented thus:

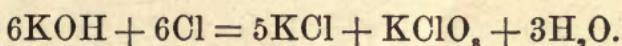


The oxygen, however, can combine with potassium chloride, KCl, to form compounds  $\text{KClO}$ ,  $\text{KClO}_2$ ,  $\text{KClO}_3$ , and  $\text{KClO}_4$ ; and the hydrochloric acid formed would combine with potassium hydroxide thus:



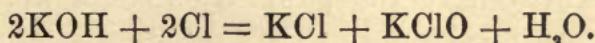
By treating potassium hydroxide with chlorine we may

therefore expect to obtain potassium chloride, KCl; some compound of potassium chloride with oxygen; and water. The above equations are given with the view of making clear what actually takes place, as has been shown by experiment. The products are different according to circumstances. If the solution of caustic potash is warm and concentrated the reaction takes place as represented, thus:



A part of the potassium chloride is oxidized to the form  $\text{KClO}_3$ , which is known as *potassium chlorate*.

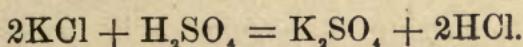
If, however, the solution is dilute, the reaction takes place thus :



In the latter case the oxidation of the potassium chloride is not carried as far as in the former. The product  $\text{KClO}$  is known as *potassium hypochlorite*.

*Potassium chlorate*,  $\text{KClO}_3$ , and *potassium hypochlorite*,  $\text{KClO}$ , bear the same relation to two compounds,  $\text{HClO}_3$  and  $\text{HClO}$ , as potassium chloride, KCl, bears to hydrochloric acid, HCl, or sodium chloride, NaCl, to hydrochloric acid. But we have seen that hydrochloric acid can be very easily obtained from sodium chloride by simply adding sulphuric acid. Potassium chloride undergoes the same change when treated with sulphuric acid. Indeed, we shall see that nearly all compounds containing sodium or potassium give up these metals when treated with sulphuric acid, and take up hydrogen in the place of them.

Treating potassium chloride with sulphuric acid this reaction takes place :

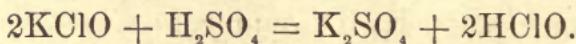


Similarly treating potassium chlorate with sulphuric acid, this reaction takes place :



The products are potassium sulphate and *chloric acid*,  $\text{HClO}_3$ . The chloric acid, however, is very unstable, and decomposes, yielding other compounds of chlorine. The acid itself can be made by taking proper precautions, but the chief interest connected with it is the fact that it decomposes very easily. Potassium chlorate, which is so closely related to it, is a very important compound. As we have already seen, it gives off its oxygen under the influence of heat. It also gives up oxygen in contact with substances which have the power to take it up. It is a powerful oxidizing agent.

*Potassium hypochlorite*,  $\text{KClO}$ , formed by passing chlorine into a dilute solution of caustic potash, is decomposed by sulphuric acid thus:



The products are potassium sulphate and *hypochlorous acid*. If a concentrated solution of potassium hypochlorite is treated with sulphuric acid, the hypochlorous acid formed at once undergoes decomposition, yielding chlorine, water, and oxygen. The acid itself is not well known. The principal compound related to it is "bleaching-powder," or the substance generally known as "chloride of lime," which is familiar to every one on account of its application as a disinfecting agent. This is made by passing chlorine into slaked lime, which from a chemical standpoint is very similar to caustic potash. Just as when chlorine acts on a dilute solution of caustic potash a mixture of potassium chloride and potassium hypochlorite is formed, so when

chlorine acts on slaked lime a mixture of calcium chloride,  $\text{CaCl}_2$ , and calcium hypochlorite,  $\text{Ca}(\text{OCl})_2$ , is formed. This mixture is bleaching-powder. By treating it with an acid it gives up chlorine, and hence it affords a convenient way of transporting chlorine. Thousands and thousands of tons of this powder are manufactured. The chlorine is passed into the lime. It is held chemically combined until it is wanted, when it can be liberated by adding an acid.

**EXPERIMENT 58.**—Dissolve 40 grams (or about  $1\frac{1}{4}$  ounces) caustic potash in 100 cc. water in a beaker-glass, and pass chlorine into it. When chlorine passes freely through the solution, thus indicating that it is no longer absorbed, stop the action. Filter the solution and allow it to cool, when crystals of potassium chlorate will be deposited, mixed with a little potassium chloride. Recrystallize from a little water. Filter off the crystals and dry them. What evidence have you that the substance is potassium chlorate? Does it give off oxygen when heated? In a dry test-tube pour two or three drops of concentrated sulphuric acid on a small crystal of the substance. Do the same with a piece of potassium chlorate from the laboratory bottle. Hold the mouth of the test-tube away from the face. What is noticed in each case?—Evaporate the solution from which the crystals of potassium chlorate have been removed. On allowing it to cool crystals will again be deposited. Take them out and recrystallize them. Does this substance give off oxygen when heated? Does it give off a gas when treated with sulphuric acid? Is this gas colored? Is it hydrochloric acid? How do you know that it is? If the gas is hydrochloric acid, what is the solid substance from which it is formed? And what is left in the test-tube?

**EXPERIMENT 59.**—Mix 20 to 30 grams (about 1 ounce) of fresh quick-lime with 50 cc. water. After the slaking is over, pass chlorine into it until the gas is no longer absorbed. Put the powder thus formed in a flask arranged as shown in Fig. 28. Pour a mixture of equal parts of sulphuric acid and water slowly through the funnel-tube. Collect by displacement of air the gas given off. What

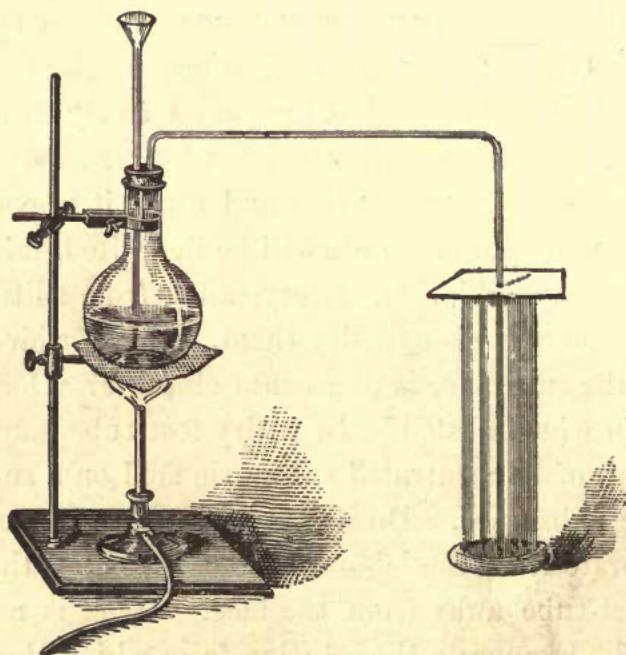
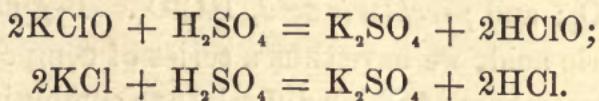


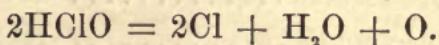
FIG. 28.

evidence have you that the gas is chlorine? In this experiment the substance first formed is bleaching-powder, or “chloride of lime.” This is decomposed by sulphuric acid, yielding chlorine. The formation of chlorine is secondary, and due to the ease with which hypochlorous acid breaks up into chlorine, oxygen, and water. The tendency of sulphuric acid to extract calcium, just as it does potassium, and to put hydrogen in its place, is at the root of

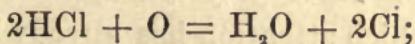
the matter. Potassium hypochlorite and potassium chloride, when treated with sulphuric acid, yield primarily hypochlorous acid and hydrochloric acid:



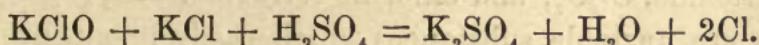
Thus far the only change that has taken place is the exchange of hydrogen for potassium. Now, however, the hypochlorous acid decomposes, yielding oxygen, water, and chlorine, probably thus:



The oxygen thus liberated would, however, act upon hydrochloric acid, if present, and set chlorine free from it:



so that, if a mixture of potassium hypochlorite and potassium chloride be treated with sulphuric acid we would expect the result to be that which is represented in this equation:



This in reality expresses what takes place, as has been proved experimentally. The decomposition of "bleaching-powder" takes place in the same way, the only difference being that in one case we have to deal with compounds of the metal potassium, while in the other we have to deal with analogous compounds of the metal calcium.

While the remaining compounds of chlorine, hydrogen, and oxygen cannot be considered here in detail, a reference to the series as a whole will serve to call to mind some important matters of general interest. There are four of

these compounds which, as far as composition is concerned, bear a very simple relation to one another. They are *hypochlorous acid*,  $\text{HClO}$ ; *chlorous acid*,  $\text{HClO}_2$ ; *chloric acid*,  $\text{HClO}_3$ ; and *perchloric acid*,  $\text{HClO}_4$ . Beginning with hydrochloric acid, we have thus a series of compounds, the successive members of which differ by one combining weight of oxygen:

Hydrochloric acid.....	$\text{HCl}$
Hypochlorous acid.....	$\text{HClO}$
Chlorous acid.....	$\text{HClO}_2$
Chloric acid.....	$\text{HClO}_3$
Perchloric acid.....	$\text{HClO}_4$

This series illustrates very clearly the *law of multiple proportions* to which attention has already been called (see *ante*, p. 26). [What is the law of multiple proportions? How does this series illustrate the law?]

**Compounds of Chlorine and Oxygen.**—There are three of these compounds, viz.: chlorine monoxide,  $\text{Cl}_2\text{O}$ ; chlorine trioxide,  $\text{Cl}_2\text{O}_3$ ; and chlorine tetroxide,  $\text{ClO}_2$  (or  $\text{Cl}_2\text{O}_4$ ). They are unstable substances which easily break up into chlorine and oxygen. They are not easily prepared in pure condition.

## CHAPTER VI.

### ACIDS—BASES—NEUTRALIZATION—SALTS.

We cannot work in a laboratory without constant reference to acids, and we have already met with a number of substances belonging to this class. It is now time for us to inquire what features these substances have in common which lead chemists to call them all acids. What is there in common between the heavy, oily liquid, sulphuric acid, the colorless gas hydrochloric acid, and the unstable substances chloric and hypochlorous acids? It is not possible for us to understand the nature of their common properties without a somewhat premature reference to a class of substances to which special attention will be called in due time. These are the *alkalies*, which are the most marked representatives of the class of substances known as *bases*. These two classes, the *acids* and the *bases*, have the power to destroy the characteristic properties of each other. When an acid is brought in contact with a base in proper proportions, the properties of both the acid and the base are destroyed. They are said to *neutralize* each other. This act of neutralization is an extremely important one, with which we constantly have to deal in chemical operations. It will therefore be advisable to study it with some care.

The most common acids are sulphuric, hydrochloric, and nitric acids. Among the more common bases are caustic

soda, caustic potash, and lime. Whenever a substance with acid properties is brought together with a substance with basic properties, some action takes place which causes the destruction of the acid properties and the basic properties.

A convenient way to recognize whether a substance has acid or basic properties is by means of certain color-changes. The dye litmus is blue. If a solution which is colored blue with litmus be treated with a drop or two of an acid, the color is changed to red. If now the red solution be treated with a few drops of a solution of a base, the blue color is restored. There are many other substances which change markedly in color, according to whether the solutions in which they are present have acid or alkaline properties. An infusion of red cabbage, for example, changes color when treated with an acid, and recovers its color when again treated with an alkali.

**EXPERIMENT 60.**—Make dilute solutions of nitric, hydrochloric, and sulphuric acids (1 part dilute acid, such as is used in the laboratory, to 50 parts water); and of caustic soda and caustic potash (about 5 grams to 100 cc. of water). Measure off about 20 cc. of each of the acid solutions. Add a few drops of a solution of blue litmus. Gradually add to each of the measured quantities of acid sufficient dilute caustic soda to cause the red color just to change to blue. As long as the solution is red it is acid. When it turns blue it is alkaline. At the turning-point it is neutral. The operation is best carried on by means of a burette, which is a graduated tube with an opening from which small quantities can be poured. A convenient shape is that represented in Fig. 29. At the lower end is a small opening. The flow of the liquid from the burette is con-

trolled by means of a small pinch-cock. It will require some practice to enable the student to know exactly when the red color disappears and the blue appears, but with practice the point can be discerned with great accuracy. Should too much alkali be allowed to get into the acid, add a small measured quantity of the acid from another burette. Having in one experiment determined how much of the solution of alkali is required to cause the red color to change to blue in operating on a given quantity of the acid solution, try the experiment again, using a different quantity of the acid solution. If the results of several experiments with the same acid and alkali be recorded it will be found that there is a definite ratio between the quantities of acid and alkali solution required to neutralize one another.

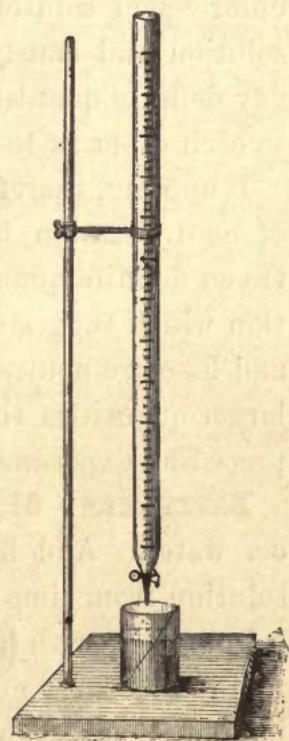


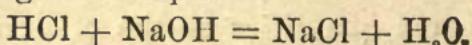
FIG. 29.

If, for example, 15 cc. of the alkali solution are required to neutralize 20 cc. of the acid solution, 18 cc. of the alkali solution will be required to neutralize 24 cc. of the acid solution, 30 cc. to neutralize 40 cc., etc. In other words, in order to neutralize a given quantity of an acid, a definite quantity of an alkali is necessary. Perform similar experiments with the other acids. Afterwards carefully examine the numerical results. Suppose it should require 15 cc. of the caustic-soda solution or 12 cc. of the caustic-potash solution to neutralize 20 cc. of the hydrochloric-acid solution. Compare the quantities of these alkali solutions necessary to neutralize equal quantities of the other acids. It will

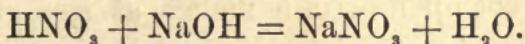
be found that, if it requires 15 cc. caustic-soda solution or 12 cc. caustic-potash solution to neutralize 20 cc. hydrochloric-acid solution, then the quantities of caustic-soda solution and caustic-potash solution required to neutralize any definite quantity of a solution of another acid will be to each other as 15 to 12.

It appears, therefore, from these experiments that the act of neutralization is a definite one, which takes place between definite quantities of acid and base. The next question which suggests itself is, What is formed when the acid and base are neutralized? To determine this we may use in larger quantities the same substances as those used in the preceding experiments.

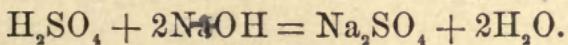
**EXPERIMENT 61.**—Dissolve 10 grams caustic soda in 100 cc. water. Add hydrochloric acid slowly, examining the solution from time to time by means of a piece of paper colored blue with litmus. As long as the solution is alkaline it will cause no change in the color of the paper. The instant it passes the point of neutralization it changes the color of the paper red; when exactly neutral it will neither change the blue to red, nor, if the color be changed to red by means of another acid, will it change it back again. When this point is reached, evaporate off the water on the water-bath to complete dryness, and see what is left. Taste the substance. Has it an acid taste? Does it suggest any familiar substance? If it is sodium chloride, how ought it to conduct itself when treated with sulphuric acid? Does it conduct itself in this way? Satisfactory evidence can be given that the substance is sodium chloride. It is not an acid nor an alkali. It is neutral. Its formation took place according to the equation



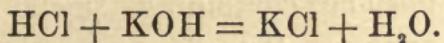
Using nitric acid and caustic soda, the product formed is sodium nitrate. Compare it with sodium nitrate from the laboratory bottle. Heat a small specimen of each in a tube closed at one end. What do you observe? Treat a small specimen of each with a little sulphuric acid in test-tubes. What do you observe? The explanation of the changes which occur in these cases will be given later. Here we are principally interested to know that the substance formed, when nitric acid acts on caustic soda, is sodium nitrate. The reaction took place thus:



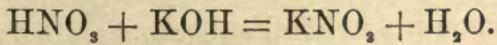
Similarly sulphuric acid and caustic soda give sodium sulphate and water, thus:



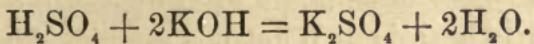
With caustic potash similar reactions take place. Hydrochloric acid and caustic potash yield potassium chloride and water :



Nitric acid and caustic potash yield potassium nitrate and water:



Sulphuric acid and caustic potash yield potassium sulphate and water :



Considering the facts just learned, we see:

- (1) That an acid contains hydrogen;
- (2) That a base contains a metal;
- (3) That when an acid acts on a base the hydrogen and metal exchange places;

(4) That the substance obtained from the acid by replacing the hydrogen by a metal is neutral;

(5) That the substance formed by replacing the metal of the base by hydrogen is water.

These statements are of general application, except statement (4), to which there are some exceptions. It is true in some cases that after replacing the hydrogen by a metal the substance has an alkaline reaction; and in other cases that the product has an acid reaction.

We have already seen that hydrochloric acid and sulphuric acid act upon certain metals, as iron and zinc, and that the action consists in giving up hydrogen and taking up metal in its place. The products of this action are the same in character as those formed by the action of acids on bases.

An *acid* is a substance containing hydrogen, which it easily exchanges for a metal when treated with a metal itself, or with a compound of a metal, called a *base*.

A *base* is a substance containing a metal combined with hydrogen and oxygen. It easily exchanges its metal for hydrogen when treated with an acid.

The products of the action of an acid on a base are, first, water, and, second, a neutral substance called a *salt*.

In the example already given sodium chloride, potassium chloride, sodium nitrate, potassium nitrate, sodium sulphate, and potassium sulphate are salts.

It may fairly be asked, What is a metal? Unfortunately for our present purpose, it is by no means an easy matter to give a satisfactory answer to this question. We can give examples of metals, such as iron, zinc, silver, calcium, magnesium, etc.; but when we attempt to discover the dis-

tinguishing features of these substances we are somewhat at a loss to state them. In general, it may be said that to the chemist any element is a metal which with hydrogen and oxygen forms a product which has the power to neutralize acids; that is to say, which has basic properties. In general, any element which has the power to enter into an acid in the place of the hydrogen is called a metal, or is said to have metallic properties. This is the sense in which the word metal is used in this book.

**Nomenclature of Acids.**—The names of the acids of chlorine illustrate some of the principles of nomenclature in use in chemistry. That acid of the series which is best known is called chloric acid. The termination *ic* is generally used in naming acids, as is seen in the names hydrochloric, sulphuric, nitric, etc. If a second acid containing the same elements exists and the proportion of oxygen contained in it is smaller than in the acid the name of which ends in *ic*, the second acid is given a name ending in *ous*. Thus *chlorous* acid contains a smaller proportion of oxygen than *chloric* acid, and the suffixes *ic* and *ous* signify that fact. We have many other examples of this use of these suffixes in the names of acids as well as in the names of compounds of other classes.

In the series of chlorine acids, however, this simple principle, which is sufficient for most cases, does not suffice. In order, therefore, to form characteristic names for the other members of the series we have recourse to prefixes. There is one acid which, so far as the proportion of oxygen contained in it is concerned, stands below chlorous acid. It is called *hypochlorous* acid, the prefix *hypo* being derived from the Greek *ὑπό*, under. Further, there is an acid which

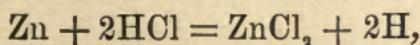
contains a larger proportion of oxygen than chloric acid. It is called *perchloric acid*, the Latin prefix *per* signifying here very or fully. It will be seen that the names of the acids vary with the proportion of oxygen contained in them.

**Nomenclature of Bases.**—As pointed out above, a base is a compound of a metal with hydrogen and oxygen. Thus, caustic soda has the formula NaOH, caustic potash KOH, lime CaO<sub>2</sub>H<sub>2</sub>, etc. They are commonly known as hydroxides. In order to distinguish between the hydroxides of the different metals, the names of the metals are put before the name hydroxide. Thus, caustic soda, NaOH, is called *sodium hydroxide*; caustic potash, KOH, is called *potassium hydroxide*; caustic lime, CaO<sub>2</sub>H<sub>2</sub>, is called *calcium hydroxide*, etc. They may be regarded as water in which a part of the hydrogen has been replaced by a metal, and indeed many of them can be made by simply bringing the corresponding metals in contact with water. Thus, as we saw in experimenting on hydrogen, when sodium or potassium is thrown on water hydrogen is evolved. The products formed were, respectively, sodium hydroxide and potassium hydroxide. These compounds are called *hydrates* by some chemists, the name implying that they are derivatives of water. The name hydroxide means simply that the substances contain hydrogen and oxygen.

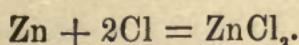
**Nomenclature of Salts.**—Theoretically every metal can yield a salt with every acid. The salts derived from a given acid receive a general name, and this general name is qualified in each case by the name of the metal contained in the salt. Thus all the salts derived from nitric acid are called *nitrates*; all the salts derived from chloric acid are called *chlorates*; the salts of sulphuric acid are called *sul-*

*phates.\** So too, further, the salts of chlorous acid are called *chlorites*; those of nitrous acid, *nitrites*; those of sulphurous acid, *sulphites*, etc., etc. It will be noticed that the terminal syllable of the name of the salt differs according to the name of the acid. If the name of the acid ends in *ic*, the name of the salt derived from it ends in *ate*. If the name of the acid ends in *ous*, the name of the salt ends in *ite*. To distinguish between the different salts of the same acid, the name of the metal contained in it is prefixed. Thus, the potassium salt of nitric acid is called potassium nitrate, the sodium salt is called sodium nitrate; the calcium salt of sulphuric acid is called calcium sulphate; the magnesium salt of nitrous acid is magnesium nitrite. The calcium salt of hypochlorous acid is calcium hypochlorite, etc., etc. [Give the name and formula of the potassium salt of perchloric acid.—Give the name and formula of the sodium salt of hypochlorous acid.—Give the name and formula of the sodium salt of nitric acid.]

If the salts of hydrochloric acid were named in accordance with the principle just explained, they would be called *hydrochlorates*. But it will be observed that these salts are identical with the products formed by direct combination of the metals with chlorine. Thus, hydrochloric acid and zinc act as represented in the equation:



while zinc and chlorine act thus:



\* If the principle were strictly applied the salts of sulphuric acid would be called *sulphurates*, but for the sake of convenience the name is shortened.

In each case the same product,  $ZnCl_2$ , is formed. But these compounds of metals with chlorine are called *chlorides* as has already been explained. Hence the name *hydro-chlorate* is unnecessary.

**Acid Properties and Oxygen.**—The observation that oxygen is generally present in acids led at one time to the belief that it is an essential constituent of these substances. Hence the name oxygen was given to it (from *'oξύς*, acid, and *γένναω*, I form). That oxygen is not essential to the existence of acid properties is shown in the case of hydro-chloric acid, and in a few other similar cases. It must be said, however, that the acid properties of substances are generally due to the presence of oxygen. Some substances with basic properties can be converted into acids by causing them to combine with oxygen.

## CHAPTER VII.

### NITROGEN.--AIR.

WE have learned that when substances burn in the air the same products are formed as when they burn in oxygen; and, further, that there is something besides oxygen present in the air which renders the burning less active than it is in oxygen alone. We have seen (Experiment 24) that if a piece of phosphorus is introduced into a vessel containing oxygen the gas slowly combines with the phosphorus, and phosphorus pentoxide is formed, which dissolves in water. We may now repeat the experiment, using air instead of oxygen.

**EXPERIMENT 62.**—Arrange the apparatus as in Fig. 4, Experiment 24. Instead of a plain tube, use one graduated into cubic centimetres. Enclose 60 to 80 cc. air in the tube over water. Arrange the tube so that the level of the water inside and outside is the same. Note the temperature of the air and the height of the barometer. Reduce the observed volume to standard conditions. Now introduce a piece of phosphorus, as in Experiment 24, and allow it to stand for twenty-four hours. Draw out the phosphorus. Again arrange the tube so that the level of the water inside is the same as that outside. Make the necessary corrections for temperature and pressure. It will be found that the volume has diminished considerably,

but that about four fifths of the gas originally put in the tube is still there. If the work is done carefully, the volume of the gas left in the tube will be to the total volume used as 79 to 100. In other words, of every 100 cc. air used 21 cc. are absorbed by phosphorus, and 79 cc. are not. The gas absorbed is oxygen, identical with the oxygen made from the oxide of mercury, manganese dioxide, and potassium chlorate. The gas left over has no chemical properties in common with oxygen. Carefully take the tube out of the vessel of water, closing the mouth with the thumb or some suitable object to prevent the contents from escaping. Turn it with the mouth upward, and introduce into it a burning stick. It is extinguished. This residual gas will not support combustion, and cannot therefore be oxygen.

The experiment just performed shows us that the air is made up by volume of 21 per cent of oxygen and 79 per cent of a gas which does not support combustion. This second constituent of the air is *nitrogen*.

**Preparation.**—The most convenient way to prepare nitrogen is to burn a piece of phosphorus in a bell jar over water.

**EXPERIMENT 63.**—Place a good-sized stoppered bell jar over water in a pneumatic trough. In the middle of a flat cork about three inches in diameter fasten a small porcelain crucible, and float this on the water in the trough. Put in it a piece of phosphorus about twice the size of a pea, and set fire to it. Quickly place the bell jar over it. At first some air will be driven out of the jar. [Why?] The burning will continue for a short time, and then gradually grow less and less active, finally stopping. On cooling, it will be found that the volume of gas is less than four fifths

the original volume, for the reason that some of the air was driven out of the vessel at the beginning of the experiment. Before removing the stopper of the bell jar see that the level of the liquid outside is the same as that inside. Try the effect of introducing successively several burning bodies into the nitrogen,—as, for example, a candle, a piece of sulphur, phosphorus, etc.

It was stated, p. 53, that oxygen is used up in the breathing process. If this is so, an animal should die if placed in an enclosed space containing a limited supply of oxygen.

**EXPERIMENT 64.**—Place a live mouse in a trap in a bell jar over water. When the oxygen is used up the mouse will die. After the animal gives plain signs of discomfort, it may be revived by taking away the bell jar and giving it a free supply of fresh air.

Anything that has the power to absorb oxygen may be used in the preparation of nitrogen from the air. To avoid contamination of the nitrogen with other substances, however, it is necessary to use something which does not form a gaseous product when burned. Metallic copper is convenient, and is not unfrequently used. It is only necessary to pass air over heated copper, when the metal combines with oxygen, forming the solid copper oxide,  $\text{CuO}$ , leaving the nitrogen uncombined. The nitrogen and oxygen which make up the air are not chemically combined with each other, but simply mixed together. It is not an easy matter to prove this statement satisfactorily, but the evidence is so strong that no chemist doubts it.

(1) If nitrogen and oxygen are mixed together, the mixture conducts itself in exactly the same way as air. The mixing is not accompanied by any phenomena indicating chemical action. We have seen that the union of

two substances is accompanied by an evolution of heat, and that whenever a chemical act takes place there is some change in the temperature of the substances. When nitrogen and oxygen are mixed there is no change in the temperature of the gases.

(2) The composition of a chemical compound is constant. The law of definite proportions is founded upon a very large number of observations, and in all cases in which we have independent evidence that chemical action takes place, it is found that the same substances combine in the same proportions to form the same product. Variation in the composition of a chemical compound is not known. The composition of the air varies slightly, according to circumstances, and this fact may be regarded as evidence that the air is not a chemical compound.

(3) Air dissolves somewhat in water. If air which has been thus dissolved be pumped out and analyzed, it will be found to have a composition different from that of ordinary air. Instead of containing 1 volume of oxygen to 4 volumes of nitrogen, it will contain 1 volume of oxygen to 1.87 volumes of nitrogen. The relative quantity of the oxygen is much larger in air which has been dissolved in water than it is in ordinary air. This is due to the fact that oxygen is more soluble in water than nitrogen is. In order, however, that one gas may dissolve more than the other, it is necessary that they should not be in chemical combination. If they were in chemical combination the compound as such would probably dissolve.

**Occurrence of Nitrogen.**—Besides being found in the free state in the air, nitrogen is found in combination in a large number of substances in nature. It is found in the nitrates, or salts of nitric acid, particularly as the potassium salt,

$\text{KNO}_3$ , known as saltpetre, and the sodium salt,  $\text{NaNO}_3$ , known as Chili saltpetre. It is also found in the form of ammonia, which is a compound of nitrogen and hydrogen, represented by the formula  $\text{NH}_3$ . Ammonia occurs in small quantity in the air, and is formed under a variety of conditions, to which reference will be made when the substance is considered. Nitrogen occurs, further, in most animal substances in chemical combination.

**Properties of Nitrogen.**—We have seen that nitrogen is a colorless, tasteless, inodorous gas. It does not support combustion, nor does it burn. [Suppose nitrogen were combustible, what would be the composition of the atmosphere?] Nitrogen not only does not combine with oxygen readily, but it does not combine with any other element except at very high temperature, and then with only a few. Just as it does not support combustion, so also it does not support respiration. An animal would die in it, not on account of any active poisonous properties possessed by it, but for lack of oxygen. In the air it serves the useful purpose of diluting the oxygen. If the air consisted only of oxygen, all processes of combustion would certainly be much more active than they now are. What the effect on animals of the continued breathing of oxygen would be, it is difficult to say.

**Other Constituents of the Air.**—Besides nitrogen and oxygen the air contains other substances, some of which are of great importance.

**EXPERIMENT 65.**—Expose a few pieces of calcium chloride on a watch-glass to the air. It gradually becomes liquid by absorbing water from the air. See Experiment 42. [What is a salt called which has the power to take up water from the air and dissolve in the water ?]

**EXPERIMENT 66.**—Expose some clear lime-water to the air. It soon becomes covered with a white crust. A similar change takes place if baryta-water be exposed in the same way. Lime-water is made by putting a few pieces of quick-lime in a bottle and pouring water upon it. The mixture is well shaken up and allowed to stand. The undissolved substance settles to the bottom, and with care a clear liquid can be poured off the top. This is lime-water, which is a solution of calcium hydroxide,  $\text{CaO}_2\text{H}_2$ , in water. Baryta-water is a solution of a similar compound of the metal barium. When these solutions are exposed to nitrogen or oxygen, or to an artificially prepared mixture of the two gases, no change takes place. Further, if air is first passed through a solution of caustic soda it no longer has the power to cause the formation of a crust on lime-water or baryta-water.

**EXPERIMENT 67.**—Arrange an apparatus as shown in Fig. 30. The wash-cylinders *A* and *B* are half filled with

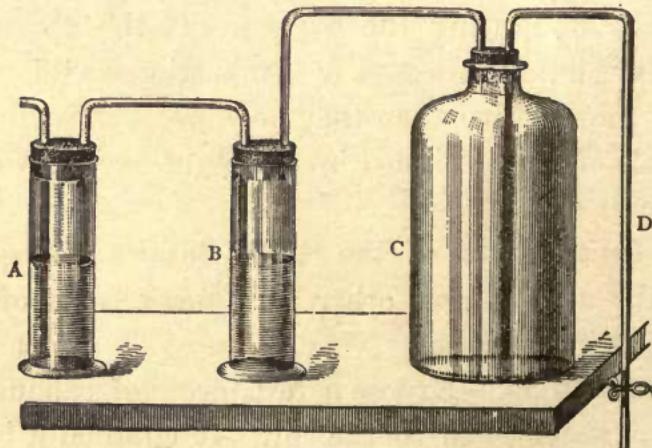


FIG. 30.

ordinary caustic-soda solution. The bottle *C* is filled with water. The tube *D*, which should be filled with water and

provided with a pinch-cock, acts as a siphon. Open the pinch-cock and let the water flow slowly out of the bottle. As it flows out air will be drawn in through the caustic-soda solution in the wash-cylinders. When the bottle is filled with air pour some water in again so that it is about a quarter full. Draw this water off as before. Now remove the stopper from the bottle, pour in 20 to 30 cc. lime-water and cork the bottle. The crust formed on the lime-water will now be hardly, if at all, perceptible. There is, therefore, something present in the air under ordinary circumstances which has the power to form a crust on lime-water or baryta-water, and which can be removed by passing the air through caustic soda. Thorough examination has shown that this is the compound which chemists call *carbon dioxide* and which is commonly known as *carbonic acid gas*. It is the substance which we obtained by burning charcoal in oxygen.

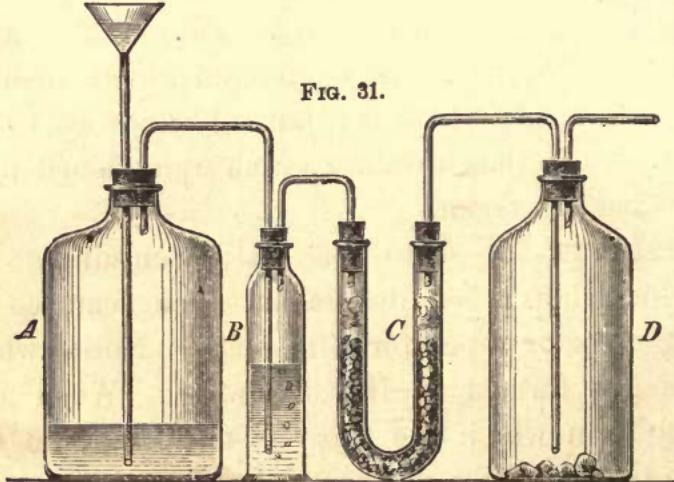
**EXPERIMENT 68.**—Into the bottle containing the air from which the carbon dioxide has been removed hold a burning stick or taper for a moment. Notice whether a crust is now formed on the lime-water. Wood and the material from which the taper is made contain carbon. Explain the formation of the crust on the lime-water after the stick of wood or taper has burned for a short time in the vessel.

**EXPERIMENT 69.**—Arrange an apparatus as shown in Fig. 31. The bottle *A* contains air. *B* contains concentrated sulphuric acid, *C* contains granulated calcium chloride, *D* is carefully dried and contains a few pieces of granulated calcium chloride and air. Pour water through the funnel-tube into *A*, the air will be forced through *B* and *C* and into

*D.* But in passing through *B* and *C* the moisture contained in it will be removed, and the air which enters *D* will be dry. After *A* has once been filled with water, empty it and fill it again, letting the dried air pass into *D*. This operation may be repeated indefinitely. The calcium chloride in *D* will not grow moist.

The preceding experiments show us that besides oxygen and nitrogen there are present in the air water, in the form of vapor, and carbon dioxide, which is a colorless gas. Wherever we examine the air these two substances are found to be present. Indeed, if we consider the circum-

FIG. 31.



stances we shall see that they must be present. Evaporation is taking place everywhere, even at low temperature, and the vapor which is formed is carried to all parts of the earth by the winds. Whenever any of our ordinary combustible substances burn in the air, carbon dioxide is formed, and, further, the process of respiration of animals also gives rise to the formation of carbon dioxide, which is given off from the lungs.

The quantity of water vapor present in the air varies between comparatively wide limits. At any given temperature the air cannot hold more than a certain quantity. When it contains this quantity it is said to be *saturated*. And if cooled down below this temperature the vapor partly condenses and appears now as water. When a vessel containing ice-water is placed in the air, that which immediately surrounds the vessel is cooled down below the point at which the quantity of water vapor present would saturate the air, and water condenses on the outside of the vessel. Every one has noticed that on a warm cloudy day more water condenses on an ice-pitcher than on a clear cool day. The water vapor present in the air has an important effect on man. The inhabitants of countries with moist climates apparently have characteristics which are not generally met with in those who inhabit countries with dry climates. The difference in the effects of moist and of dry air on an individual is well known.

Water vapor is lighter than air; hence clouds rise and float in the air. When air which is charged with water vapor comes in contact with cooler air, the vapor condenses and falls as rain.

The quantity of water vapor in a given volume of air can be determined by drawing the air through a weighed tube containing calcium chloride. This will absorb the water and increase in weight, and the increase in weight will represent the quantity of water in the volume of air drawn through the tube.

The quantity of carbon dioxide in the air is relatively very small, being about 3 parts in 10,000 parts of air. It varies slightly according to the locality and the season. It is essential to the growth of all plants.

Besides nitrogen and oxygen, carbon dioxide and water, the air contains a small quantity of ammonia (see p. 138) and a large number of other substances in very small quantities.

## CHAPTER VIII.

### COMPOUNDS OF NITROGEN WITH HYDROGEN AND OXYGEN.

**General Conditions which Give Rise to the Formation of the Simpler Compounds of Nitrogen.**—We have seen that nitrogen is an inactive element, showing little tendency to combine with other elements. It is nevertheless an easy matter to get compounds of nitrogen with many other elements, and among these compounds, some of those which it forms with hydrogen and oxygen are the most important.

Whenever a compound containing carbon, hydrogen, and nitrogen is heated in a closed vessel, so that the air does not have access to it and it cannot burn up, the nitrogen passes out of the compound, not as nitrogen, but in combination with hydrogen, in the form of the compound called *ammonia*. Nearly all animal substances contain carbon, hydrogen, oxygen, and nitrogen, and many of them give off ammonia when heated. Similarly compounds containing carbon, oxygen, and hydrogen, even though they be thoroughly dry, when heated, give off oxygen in combination with hydrogen in the form of water. Some animal substances give off ammonia when they undergo decomposition in the air. The coal which is used for making

illuminating gas contains some hydrogen and nitrogen in chemical combination, and when the coal is heated ammonia is given off.

When animal substances undergo decomposition in the presence of a base where the temperature is comparatively high, the nitrogen combines with oxygen and the metal of the base. Either a nitrite or a nitrate is formed; that is to say, either a salt of nitrous acid,  $\text{HNO}_2$ , or of nitric acid,  $\text{HNO}_3$ . In some countries where the conditions are favorable to the process, immense quantities of nitrates are found, chiefly potassium nitrate, or saltpetre,  $\text{KNO}_3$ , and sodium nitrate, or Chili saltpetre,  $\text{NaNO}_3$ . The change of the animal substances to the form of nitrates is probably caused by myriads of minute living organisms. How they effect the change is not known. From the salts of nitric acid which are found in nature, nitric acid itself can easily be extracted.

Nearly all the compounds of nitrogen with which we shall have to deal are made either from ammonia or from nitric acid.

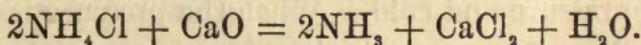
**Ammonia,  $\text{NH}_3$ .**—The conditions under which ammonia is formed have been mentioned. The chief source at present is the “ammoniacal liquor” of the gas-works. This is the water through which the gas has been passed for the purpose of removing the ammonia. It contains ammonia in solution. By adding hydrochloric acid to this liquid, *ammonium chloride*, which is a compound of the acid with ammonia, is formed. This is the well-known substance *sal ammoniac*. This name was first applied to common salt found in the Libyan desert in the neighborhood of the Temple of Jupiter Ammon. A confusion of terms afterwards led to the application of the name ammonium

chloride. As ammonium chloride, or sal ammoniac, is the most common compound containing ammonia, it is used in the laboratory for making ammonia. For this purpose it is only necessary to treat the salt with an alkali.

**EXPERIMENT 70.**—To a little ammonium chloride on a watch-glass add a few drops of a strong solution of caustic soda, and notice the odor of the gas given off. Do the same thing with caustic potash. Mix small quantities of ammonium chloride and lime in a mortar and notice the odor. The odor is that of ammonia. Has the ammonium chloride this odor?

**Preparation of Ammonia.**—Ammonia is best prepared by mixing quick-lime and ammonium chloride in the proportion of 2 parts of the former to 1 part of the latter; and gently heating the mixture.

It has been shown that besides the ammonia, which is given off in the form of a gas, calcium chloride,  $\text{CaCl}_2$ , and water are formed in this reaction. It is represented thus:



This curious reaction will be considered more fully after the nature of ammonia has been studied.

**EXPERIMENT 71.**—Arrange an apparatus as shown in Figure 27, p. 106. In the flask put a mixture of 100 grams quick-lime and 50 grams ammonium chloride. Heat on a sand-bath. After the air is driven out, the gas will be completely absorbed by the water in the first Wolff's flask. Disconnect the delivery-tube from the series of Wolff's flasks, and connect with another tube bent upward. Collect some of the escaping gas by displacement of air, *placing the vessel with the mouth downward*, as the gas is much

lighter than air. The arrangement is shown in Fig. 32.

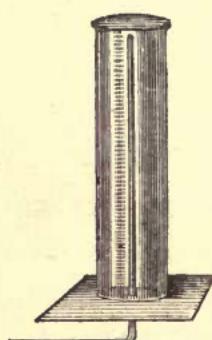


FIG. 32.

The vessel in which the gas is collected should be dry, as water absorbs ammonia very readily. Hence, also, it cannot be collected over water. In the gas collected introduce a burning stick or taper. Ammonia does not burn in air, nor does it support combustion. In working with the gas great care must be taken to avoid inhaling it in any

quantity. After enough has been collected in cylinders to exhibit the chief properties, connect the delivery tube again with the series of Wolff's flasks, and pass the gas through the water as long as it is evolved.

From the observations made in the experiments just performed, we see that ammonia is a colorless, transparent gas. It has a very penetrating characteristic odor. In concentrated form it causes suffocation. Its specific gravity is 0.586; that is to say, it is but little more than half as heavy as air. It can easily be compressed to the liquid form by pressure and cold. When the pressure is removed from the liquefied ammonia, it passes back to the form of gas. In so doing it absorbs heat. These facts are taken advantage of for the artificial preparation of ice. Carré's ice-machine is used for this purpose.

Ammonia does not burn in the air, but does burn in oxygen. It is absorbed by water in very large quantity. One volume of water at the ordinary temperature dissolves about 600 volumes of ammonia gas, and at  $0^{\circ}$  about 1000 volumes.

[PROBLEM.—A litre of air at  $0^{\circ}$  weighing 1.293 grams, and the specific gravity of ammonia gas being 0.586, how much would a litre of water increase in weight by being saturated with ammonia at  $0^{\circ}$ ?]

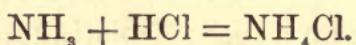
The solution of ammonia in water is what we commonly have to deal with under the name of ammonia. It is called "Spirits of Hartshorn" in common language. The solution has the odor of the gas. It loses all its gas when heated to the boiling temperature. The solution shows a strong alkaline reaction and has the power to neutralize acids.

**EXPERIMENT 72.**—Put 100 cc. *dilute* ammonia solution in an evaporating-dish. Try its effect on red litmus paper. Slowly add dilute hydrochloric acid until the alkaline reaction is destroyed and the solution is neutral. Evaporate to dryness on a water-bath. Compare the substance thus obtained with sal-ammoniac, or ammonium chloride. Taste them. Heat them on a piece of platinum foil. Treat them with a caustic alkali. Treat with a little concentrated sulphuric acid in dry test-tubes. Do they appear to be identical? The product is ammonium chloride,  $\text{NH}_4\text{Cl}$ . Similarly sulphuric acid and ammonia yield ammonium sulphate; nitric acid and ammonia yield ammonium nitrate, etc.

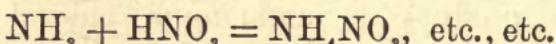
**EXPERIMENT 73.**—Fill a cylinder with ammonia gas, and another of the same size with hydrochloric-acid gas. Bring them together with their mouths covered. Quickly remove the covers, when a dense white cloud will appear in and about the cylinders. This will soon settle on the walls of the vessels as a light white solid. It is ammonium chloride. Thus, from two colorless gases we get a solid substance by an act of chemical combination. Heat is evolved in the act of combination.

We have seen that the alkalies are strong bases, and that bases are compounds of metals with hydrogen and oxygen. Certainly those substances which show an alkaline reaction

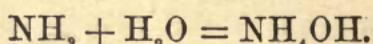
are compounds of metals with hydrogen and oxygen. But in the solution of ammonia in water we have a substance which shows an alkaline reaction and which acts in nearly all respects very much like a solution of sodium hydroxide or potassium hydroxide. The salts which ammonia forms with acids are very similar to sodium and potassium salts. What is the substance which has the alkaline reaction? and what are the salts which are formed by the action of acid on ammonia? In the first place, it has been found that when an acid acts on ammonia the two combine directly without the formation of anything but the salt. Thus ammonia and hydrochloric acid form ammonium chloride :



Ammonia and nitric acid form ammonium nitrate :

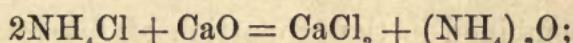


On comparing the formulas of ammonium salts with those of potassium and sodium salts we see that, while in the potassium and sodium salts the metals potassium and sodium take the place of the hydrogen of the acids, in the ammonium salts the place of the acid hydrogen appears to be taken by a compound of the formula  $\text{NH}_4$ . It has been suggested, and the idea has been generally accepted, that when ammonia gas dissolves in water an unstable compound of the formula  $\text{NH}_4\text{OH}$  is formed thus :

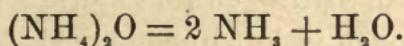


In this hydroxide, as in the salts of ammonia, the compound  $\text{NH}_4$  appears to play the part of a metal. The com-

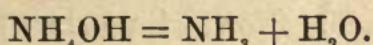
pound  $\text{NH}_4$  is, however, wholly hypothetical. As it appears to be this which plays the part of a metal in the solution as well as in the salts, the name *ammonium* has been given to it, the ending *ium* being that which is usually given to signify metallic character. We speak, then, of *ammonium salts*, just as we speak of potassium or sodium or calcium salts. In the ammonium salts the hypothetical compound metal ammonium,  $\text{NH}_4$ , is assumed to be present. If, however, we attempt to set it free or to set its hydroxide free, we get ammonia. On treating ammonium chloride with lime, if any action takes place at all we would expect it to be that represented by the equation



that is to say, we would expect the calcium and ammonium and the oxygen and the chlorine to exchange places. Perhaps this is the action which takes place at first. But the compound  $(\text{NH}_4)_2\text{O}$ , or ammonium oxide, if formed at all, breaks up at once into ammonia and water, thus:



So, too, if ammonium hydroxide,  $\text{NH}_4\text{OH}$ , is present in the solution of ammonia in water, it breaks up very readily into ammonia and water under the influence of gentle heat :



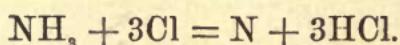
**Composition of Ammonia.**—By oxidation under the proper conditions it is possible to convert the hydrogen of ammonia into water and leave the nitrogen in the free state.

As water and nitrogen are the only products formed, and the quantity of oxygen used up in the oxidation is equal to the quantity of oxygen found in the water formed, it follows that nitrogen and hydrogen are the only elements contained in ammonia.

When electric sparks are passed for some time through a mixture of nitrogen and hydrogen, some ammonia is formed. Conversely, when electric sparks are passed for a time through ammonia, nitrogen and hydrogen are obtained.

If, in the oxidation of a known quantity of ammonia, the water formed and the nitrogen left uncombined be accurately determined, it will be found that in ammonia the elements are combined in the proportion of *fourteen parts by weight of nitrogen to three parts by weight of hydrogen*. This fact is expressed by the formula  $\text{NH}_3$ ; 14 being the combining weight of nitrogen.

The proportion by volume in which the two elements combine may be determined by the following method. When ammonia is treated with chlorine it is decomposed, the great affinity of hydrogen for chlorine causing them to unite. The nitrogen is left uncombined. The reaction is represented thus :

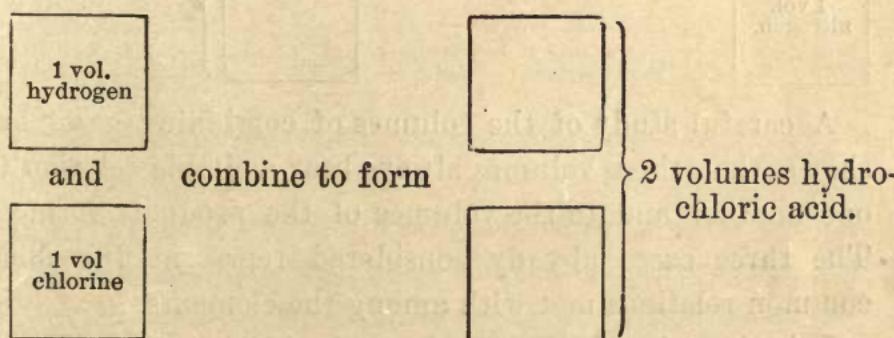


Hydrogen and chlorine unite in equal volumes, as we have already learned. Now, if we start with a measured volume of chlorine and add ammonia to it until it is all used up, we know that the volume of hydrogen which has been extracted from ammonia is equal to the volume of chlorine with which we started. If we measure the nitrogen

left over, we know what volume of nitrogen was combined with the volume of hydrogen already determined. We would find that the volume of nitrogen to that of the hydrogen with which it was combined is as 1 to 3; or *in ammonia 1 volume of nitrogen is combined with 3 volumes of hydrogen.*

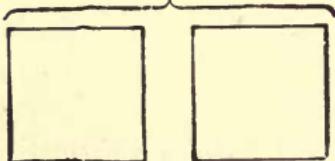
When a given volume of ammonia is decomposed into nitrogen and hydrogen, the mixture occupies just twice the volume that the ammonia did; or, if a mixture of nitrogen and hydrogen in the proper proportions to form ammonia be caused to combine, the ammonia formed would occupy one half the volume occupied by the mixture of gases.

**Relations between the Volumes of Combining Gases.**—In studying the volume relations of hydrogen, chlorine, and hydrochloric acid with reference to one another, we found that when hydrogen and chlorine combine one volume of the one combines with one volume of the other, and two volumes of the product are formed. These facts may be represented graphically thus:

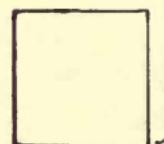
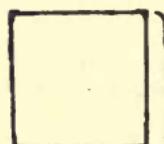


When hydrogen and oxygen combine, two volumes of hydrogen combine with one volume of oxygen; and the three volumes of gas thus combined form two volumes of water vapor:

2 volumes hydrogen



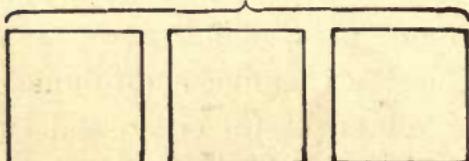
and combine to form



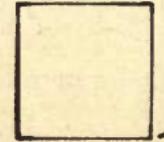
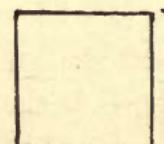
2 volumes  
water vapor.

Finally, we have just learned that one volume of nitrogen combines with three volumes of hydrogen to form two volumes of ammonia:

3 volumes hydrogen



and combine to form



2 volumes  
ammonia.

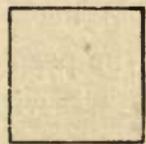
A careful study of the volumes of combining gases has shown that these volumes always bear a simple relation to one another and to the volumes of the products formed. The three cases already considered represent the more common relations met with among the elements.

It is clear that the three elements chlorine, oxygen, and nitrogen influence hydrogen differently. One volume of chlorine can hold in combination but one volume of hydrogen. One volume of oxygen can hold in combination two volumes of hydrogen, and at the same time cause a condens-

sation of volume from three volumes of gas to two. One volume of nitrogen can hold in combination three volumes of hydrogen, and, at the same time, cause the condensation of four volumes of gas to two.

**Relations between the Specific Gravities of Gases and their Combining Weights.**—Attention has already been called to the fact that the weights of equal volumes of hydrogen, chlorine, and oxygen stand in the same relation to one another as the combining weights. Nitrogen is no exception to this rule. The specific gravity of nitrogen is 0.967. One litre of nitrogen weighs 1.2553 grams. The specific gravity of hydrogen is 0.0693; and the weight of a litre of hydrogen is 0.089578. But  $0.0693 : 0.967 :: 1 : 14$  and, of course,  $0.089578 : 1.2553 :: 1 : 14$ . The accepted combining weight of nitrogen is 14.

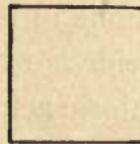
These remarkable facts may be represented graphically thus:



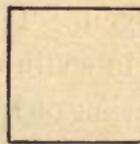
1 litre of hydrogen  
weighs 0.089578 gr.



1 litre of chlorine  
weighs 3.17 gr.



1 litre of oxygen  
weighs 1.429 gr.



1 litre of nitrogen  
weighs 1.2553 gr.

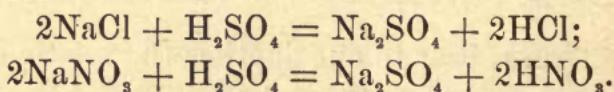
These figures bear to one another the relations expressed by the figures 1, 35.4, 16, and 14. But these last figures very nearly express the combining weights of the elements. It appears, therefore, that *the combining weights of some of the gaseous elements bear to one another the same relations as the weights of equal volumes of the gases*.

Observations of this kind, together with other observations on the conduct of gases, have led to a very important conception in regard to the nature of gases and the constitution of matter. This will be considered further on. For the

present it will be best to confine our attention to the facts, so that when we begin to speculate in regard to the hidden causes of the phenomena observed we shall have some foundation for our speculations to rest upon.

**Nitric Acid, HNO<sub>3</sub>.**—To effect the direct union of nitrogen with oxygen and hydrogen is not easier than to effect the direct union of nitrogen with hydrogen to form ammonia. Nevertheless, the silent and continuous action of minute organisms in the soil is always tending to transform the waste products of animal life into compounds closely allied to nitric acid. The process of *nitrification* has already been referred to. It is plainly an oxidizing process. In general, by oxidation the nitrogen of animal substances is converted into nitric acid, while by reduction it is converted into ammonia.

**Preparation of Nitric Acid.**—In preparing nitric acid we always start with a nitrate, and replace the metal by hydrogen. This is done in the same way that the metal sodium in sodium chloride is replaced by hydrogen in the preparation of hydrochloric acid,—viz., by treating the salt with a strong acid.



The action is due to the difference between the strengths of the two acids, sulphuric and nitric acids. We call one acid stronger than another when the former decomposes the salts of the latter, appropriating the metal and setting the weaker acid free. In this sense sulphuric acid is a *strong acid*, stronger than either hydrochloric or nitric acid. The designation is not an accurate one, for the relative strengths of the acids vary somewhat with surrounding

conditions, so that an acid may be strong under some circumstances and comparatively weak under others. For most cases which we shall have to deal with in this stage of our study the expression is satisfactory, and it will facilitate our study to recognize the fact that a strong acid decomposes the salt of a weak acid, setting the latter free.

**EXPERIMENT 74.**—Arrange an apparatus as shown in Fig. 33. In the retort put 25 grams sodium nitrate (Chili

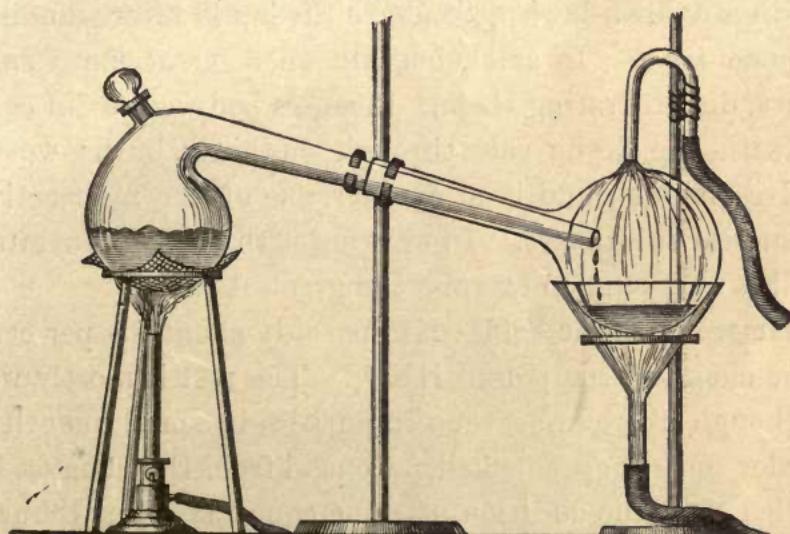


FIG. 33.

saltpetre) and 15 grams concentrated sulphuric acid. On gently heating, nitric acid will distil over, and be condensed in the receiver. After the acid is all distilled off, remove the contents of the retort. Recrystallize the substance from water, and compare it with the sodium sulphate obtained in the preparation of hydrochloric acid. (See Experiment 57.) In the latter stage of the operation the vessels become filled with a reddish-brown gas. The acid which is collected has a somewhat yellowish color.

Pure nitric acid is a colorless liquid. It gives off color-

less fumes when exposed to the air. When boiled it undergoes slight decomposition into oxygen, water, and compounds of nitrogen and oxygen. One of these compounds is colored, and it is this which is noticed in the above experiment, and whenever strong nitric is boiled. Nitric acid undergoes a similar decomposition when exposed to the action of the direct rays of the sun. In consequence of this decomposition bottles containing strong nitric acid always contain a reddish-brown gas above the liquid after standing for some time. It acts violently on a great many substances, disintegrating them. It causes bad wounds in contact with the flesh; eats through clothing; burns wood; dissolves metals; and is altogether one of the most active of chemical substances. In working with the concentrated acid it is necessary to exercise the greatest care.

Commercial nitric acid contains only about 68 per cent of the chemical compound  $\text{HNO}_3$ . The rest is mostly water, though there are several impurities in small quantity. In order to get concentrated pure acid from this it must be distilled after the addition of some concentrated sulphuric acid.

**EXPERIMENT 75.**—Mix together 400 grams concentrated sulphuric acid and 80 grams ordinary concentrated nitric acid. Pour the sulphuric acid into the nitric acid. Distil the mixture from a retort arranged as in Experiment 74, taking care to keep the neck of the retort cool by placing filter-paper moistened with cold water on it. Use the acid thus obtained for the purpose of studying the properties of pure nitric acid.

In consequence of the ease with which nitric acid decomposes, giving up oxygen, it is an excellent oxidizing agent, and is much used in the laboratory in this capacity. To

illustrate its oxidizing power, the following experiments may be performed :

**EXPERIMENT 76.**—Pour concentrated nitric acid into a wide test-tube, so that it is about one fourth filled. Heat the end of a stick of charcoal of proper size, and, holding the other end with a forceps, introduce the heated end into the acid. It will continue to burn with a bright light, even though it be placed below the surface of the liquid. The action is oxidation. The charcoal in this case finds the



FIG. 34.

oxygen in the acid, and not in the air. Great care must be taken in performing this experiment. The charcoal should not come in contact with the sides of the test-tube. A large beaker glass should be placed beneath the test-tube, so that, in case it should break, the acid would be caught and prevented from doing harm. The arrangement of the apparatus is shown in Fig. 34.

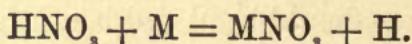
The gases given off from the tube are offensive and poisonous. Hence this as well as all other experiments with

nitric acid should be carried on under a hood in which the draught is good.

**EXPERIMENT 77.**—Boil a little strong nitric acid in a test-tube in the upper part of which some horse-hair has been introduced in the form of a stopper. The horse-hair will take fire and burn, and leave a white residue. Hold the test-tube with a forceps over a vessel to catch the contents should the tube break.

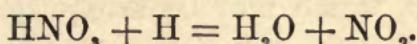
**EXPERIMENT 78.**—In a small flask put a few pieces of granulated tin. Pour on this just enough strong nitric acid to cover it. Heat gently over a small flame. Soon action will take place. Colored gases will be evolved, the tin will disappear, and in its place will be found a white powder. This consists mostly of tin and oxygen. (See Experiment 15.)

The experiments just performed illustrate the oxidizing power of nitric acid. Like other acids, nitric acid forms salts with the metals. These may be made by treating the metals themselves with the acid, but in this case the formation of the salt is accompanied by another kind of action which is quite characteristic of nitric acid. When nitric acid acts on most metals hydrogen is first displaced by the metal, and nitrates are formed, as we would expect. Thus, if *M* represents a metal, and it be brought into nitric acid, we should expect the reaction to take place as represented in the equation

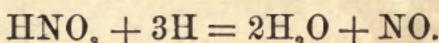


But as nitric acid gives up oxygen readily, it appears that the displaced hydrogen combines with oxygen from the acid reducing it, and causing the formation of compounds of oxygen and nitrogen containing a smaller proportion of

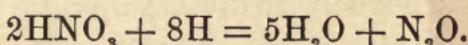
oxygen than the acid. Thus, one product of the action is the compound  $\text{NO}_2$ , called nitrogen peroxide. Its formation may be represented thus :



Another compound which is frequently formed is nitric oxide,  $\text{NO}$ . Its formation may be represented thus :



The reduction may be carried still farther, yielding nitrous oxide,  $\text{N}_2\text{O}$ :



Under other circumstances the reduction may be carried still farther, the last product of the action being ammonia,  $\text{NH}_3$ .

As nitrogen peroxide is a colored gas and some of it is always formed when nitric acid acts on metals in the air, the presence of the reddish-brown substance observed in the experiments already performed with nitric acid will be readily understood.

**EXPERIMENT 79.**—Dissolve a few pieces of copper foil in ordinary commercial nitric acid diluted with about half its volume of water. The operation should be carried on in a good-sized flask and under an efficient hood. When the copper has disappeared, pour the blue solution into an evaporating-dish, and evaporate down to crystallization. Compare the substance, thus obtained with copper nitrate.—Heat specimens of each.—Treat small specimens with sulphuric acid.—Do the two substances appear to be identical?

**EXPERIMENT 80.**—Heat specimens of potassium nitrate,

sodium nitrate, lead nitrate, and any other nitrates which may be available. All are decomposed giving off oxygen, in some cases mixed with oxides of nitrogen, among which is nitrogen peroxide, which may be recognized by its color. *All salts of nitric acid are decomposed by heat, and all are soluble in water.*

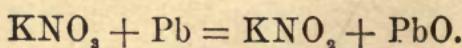
**EXPERIMENT 81.**—Try the solubility in water of the nitrates used in the last experiment.

The formation of ammonia by reduction of nitric acid may be shown by the following experiment.

**EXPERIMENT 82.**—In a good-sized test-tube treat a few pieces of granulated zinc with dilute sulphuric acid. What is evolved? Prove it. Now add drop by drop dilute nitric acid. The hydrogen ceases to be given off. Pour the contents of the tube into an evaporating-dish and evaporate the liquid. Put the residue into a test-tube and add caustic-soda solution, when the smell of ammonia will be noticed. Try the action of the gas on red litmus paper. Moisten the end of a glass rod with a little hydrochloric acid and hold it in the tube. White fumes are seen. What are they? Do the same with nitric acid. What are the fumes in this case?

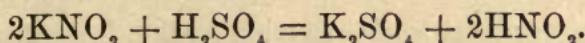
*Aqua regia* is made by mixing together concentrated nitric and hydrochloric acids. It is an excellent solvent.

**Nitrous Acid,  $\text{HNO}_2$ .**—Among the reduction products of nitric acid is nitrous acid,  $\text{HNO}_2$ . This acid is most easily prepared in the form of a salt by reducing a nitrate. Thus, if potassium nitrate,  $\text{KNO}_3$ , be melted together with metallic lead, the lead extracts a part of the oxygen and leaves potassium nitrite,  $\text{KNO}_2$ .

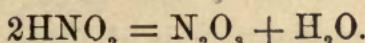


**EXPERIMENT 83.**—Heat together in a shallow iron plate 25 grams potassium nitrate and about 50 grams metallic lead. When both are melted stir them together as thoroughly as possible. After the mass is cooled down, break it up and treat with water in a flask. The potassium nitrite will dissolve, while the lead oxide and unused lead will not dissolve. Filter off. Add a little sulphuric acid to some of the solution. A colored gas will be given off. See whether a solution of potassium nitrate acts in the same way.

Nitrous acid itself is not known, though its salts are well known. When a strong acid is added to a solution of a nitrite, the salt is decomposed and *nitrogen trioxide* or *nitrous anhydride*,  $\text{N}_2\text{O}_3$ , is given off. The reaction will be readily understood. The tendency of the strong acid is to set the weak acid free, as when sodium chloride is treated with sulphuric acid, and potassium nitrate is treated with sulphuric acid. Were the action in this case analogous, it would be represented thus :



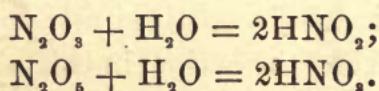
We should get nitrous acid ; but instead of this we get a substance which is nitrous acid less the elements of water :



This tendency on the part of compounds which contain hydrogen and oxygen to decompose with formation of water is very commonly observed. We have already had to deal with a case of the kind in ammonium hydroxide. This substance, which probably exists in solution in water, yields when heated, ammonia and water. Many compounds which do not break up in this way at ordinary tempera-

tures do so at elevated temperatures. This decomposition is to be ascribed to the strong affinity of hydrogen for oxygen. In complex compounds several forces are at work to keep the constituents in equilibrium. If the affinity of hydrogen for oxygen is much stronger than the other forces at work, the equilibrium is disturbed, and decomposition takes place. At least, this is the thought which naturally suggests itself by way of partial explanation of the phenomena.

**Anhydrides.**—A compound which, in its composition, bears to an acid the relation which nitrogen trioxide,  $\text{N}_2\text{O}_5$ , bears to nitrous acid,  $\text{HNO}_2$ , is called an *anhydride*. Thus we have *nitrous anhydride*,  $\text{N}_2\text{O}_5$ ; *nitric anhydride*,  $\text{N}_2\text{O}_5$ , etc. Nitric anhydride bears the same relation to nitric acid that nitrous anhydride bears to nitrous acid.



In more general terms, it may be said that any oxide which, when brought together with water, forms an acid by direct combination, is an anhydride. We shall meet with some other examples of this class of compounds further on.

**The Oxides of Nitrogen.**—In the account given above of the transformations of nitric acid under the influence of reducing agents, five compounds of nitrogen and oxygen were mentioned. These are nitrogen peroxide,  $\text{NO}_2$ ; nitric oxide,  $\text{NO}$ ; nitrous oxide,  $\text{N}_2\text{O}$ ; nitrous anhydride,  $\text{N}_2\text{O}_5$ , and nitric anhydride,  $\text{N}_2\text{O}_5$ . Arranging these compounds in a series, beginning with that one which contains the smallest proportion of oxygen, and considering in each case the quantity of oxygen which is combined with two combining weights (*i.e.*, twenty-eight parts by weight) of nitro-

gen, we see that the series affords a striking illustration of the facts from which the law of multiple proportions is deduced. The series is:

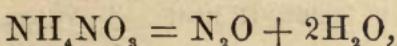
Nitrous oxide.....	$\text{N}_2\text{O}$
Nitric oxide.....	NO or $\text{N}_2\text{O}_2$
Nitrogen trioxide.....	$\text{N}_2\text{O}_3$
Nitrogen peroxide....	$\text{NO}_2$ or $\text{N}_2\text{O}_4$
Nitric anhydride.....	$\text{N}_2\text{O}_5$

It will be seen that the quantities of oxygen combined with twenty-eight parts of nitrogen are 16, 32, 48, 64, and 80.

[What other series of compounds have we already had to deal with which illustrates the law of multiple proportions almost equally strikingly?]

Of the oxides of nitrogen, only three need be considered, and after what has already been said they need be considered only briefly.

**Nitrous Oxide,  $\text{N}_2\text{O}$ .**—This compound is formed by reduction of nitric acid when the acid acts upon metals and the degree of concentration and the temperature are favorable. It is usually prepared by heating ammonium nitrate,  $\text{NH}_4\text{NO}_3$ . The decomposition takes place as represented, thus:



the products being nitrous oxide and water. In this reaction we see exhibited the tendency of hydrogen and oxygen to combine at elevated temperature. At ordinary temperatures this affinity is not strong enough to cause a disturbance of the equilibrium of the parts of the compound.

As the temperature is elevated it becomes stronger and stronger, until finally they combine and the decomposition above represented takes place.

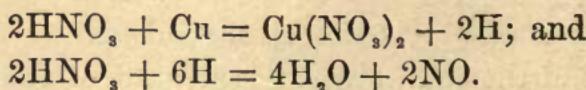
**EXPERIMENT 84.**—In a retort heat 10 to 15 grams crystallized ammonium nitrate until it has the appearance of boiling. Do not heat higher than is necessary to secure a regular evolution of gas. Connect a wide rubber tube directly with the neck of the retort and collect the evolved gas over water, as in the case of oxygen. It supports combustion almost as well as pure oxygen. Try experiments with wood, a candle, and a piece of phosphorus.

The gas is colorless and transparent. It has a slightly sweetish taste. It is somewhat soluble in water, so that when collected over water there is always considerable loss. When inhaled it causes a kind of intoxication, which is apt to show itself in the form of hysterical laughing. Hence the gas is generally known as *laughing-gas*. Inhaled in larger quantity it causes unconsciousness and insensibility to pain. It is therefore used to prevent pain in minor surgical operations, as, for example, in pulling teeth.

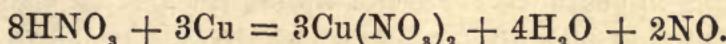
**Nitric Oxide, NO.**—This gas, as has been stated, is formed when nitric acid acts upon some metals, as copper. The action is believed to involve two changes.

- (1) The copper displaces the hydrogen of the acid, and copper nitrate is formed; and
- (2) The hydrogen acts upon the nitric acid, reducing it and forming nitric oxide.

These two stages are represented thus:



The two equations may be combined in one, when we have



**EXPERIMENT 85.**—Arrange an apparatus as shown in Fig. 35. In the flask put a few pieces of copper foil. Cover this with water. Now add slowly, waiting each time for the action to begin, *ordinary* concentrated nitric acid. When enough nitric acid has been added gas will be evolved. If the acid is added rapidly, it not unfrequently happens that the evolution of gas takes place too rapidly, so that the liquid is forced out of the flask through the funnel-tube. This can be avoided by not being in a hurry. At first the vessel becomes filled with a reddish-brown gas, but soon the gas evolved becomes colorless. Collect over water two or three vessels full. The gas collected is principally nitric oxide, NO, though it is frequently mixed with a considerable quantity of nitrous oxide.

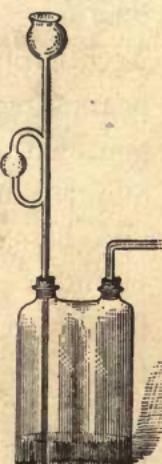
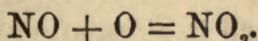


FIG. 35.

Nitric oxide is a colorless, transparent gas. Its most remarkable property is its power to combine directly with oxygen when the two are brought together. The act of combination is not accompanied by the appearance of light, though heat is evolved. The reaction which takes place is represented by the equation



The product is nitrogen peroxide, and this at ordinary temperatures is a reddish-brown gas.

**EXPERIMENT 86.**—Turn one of the vessels containing

colorless nitric oxide with the mouth upward and uncover it. The colored gas is at once seen, presenting a very striking appearance. Do not inhale the gas. Perform the experiments with nitric oxide where there is a good draught.

Nitric oxide does not burn, and does not support combustion. When we consider the fact that nitrous oxide,  $\text{N}_2\text{O}$ , supports combustion almost as well as oxygen, it appears strange that another compound of nitrogen and oxygen, containing twice as much oxygen relatively to the same quantity of nitrogen, should not support combustion. This is to be explained by the relative stability of the two compounds. In the case of nitrous oxide, the oxygen is not firmly held in combination; the equilibrium established between the forces at work is not a stable one. Hence, when a substance which has a strong affinity for oxygen is brought in contact with it, the equilibrium is disturbed, or the oxide is decomposed. On the other hand, in nitric oxide the arrangement of the parts is a more stable one. The oxygen, although present in larger quantity than in nitrous oxide, is held more firmly, and cannot easily be extracted. The gas does not support combustion.

**Nitrogen Peroxide,  $\text{NO}_2$ .**—This gas is made by direct combination of nitric oxide with oxygen, as seen in the last experiment. It has a disagreeable smell and is poisonous. It gives up a part of its oxygen quite easily, and is hence useful as an oxidizing agent. We shall hereafter see that in the manufacture of sulphuric acid the oxidizing power of nitrogen peroxide is utilized in a very beautiful and interesting way. When it gives up oxygen, it is changed to nitric oxide,  $\text{NO}$ . If air is present, nitric oxide is changed back again to nitrogen peroxide, which may again give up oxygen, again yielding nitric oxide, and so on indefinitely.

It will thus be seen that these oxides of nitrogen may be made to serve the purpose of transferring oxygen from the air to other substances.

**Summary.**—The simpler nitrogen compounds are made either from ammonia or nitric acid. Ammonia is formed in nature by the spontaneous decomposition of animal substances. It is also formed by heating substances which contain carbon, hydrogen, and nitrogen. The principal source is the “ammoniacal liquor” of the gas-works.

Nitric acid is formed in nature as the potassium or sodium salt, by the action of certain organisms on substances containing nitrogen.

Ammonia is prepared from an ammonium salt by treating it with a strong base. Ammonium chloride and lime are commonly used.

With acids ammonia forms salts which are known as ammonium salts, and in which the compound  $\text{NH}_4$  is supposed to act the part of a metal. This hypothetical metal is called *ammonium*.

Ammonia consists of 14 parts of nitrogen to 3 parts of hydrogen. The gases are combined in the proportion of 1 volume of nitrogen to 3 volumes of hydrogen. The 4 volumes thus combined condense to 2 volumes of ammonia.

There is always a simple relation between the volumes of combining gases and the volume of the compound formed.

A comparison of the specific gravities of the gaseous elements shows that these bear to one another the same relation as the combining weights.

Nitric acid is prepared from a nitrate by treating it with sulphuric acid. It is comparatively unstable, giving up oxygen easily. With metals it yields salts, but the hydrogen evolved acts upon a part of the acid, forming reduction

products, among which are nitrous oxide,  $N_2O$ ; nitric oxide,  $NO$ ; nitrous anhydride,  $N_2O_3$ ; and nitrogen peroxide,  $NO_2$ . Under some circumstances, the action of hydrogen may even go far enough to form ammonia. Nitrous acid itself is unstable, breaking up into the anhydride,  $N_2O_3$ , and water.

Anhydrides are substances which, when brought together with water, combine with it to form acids.

Though nitrous oxide is formed by reduction of nitric acid, it is best prepared in pure condition by heating ammonium nitrate. It supports combustion well.

Nitric oxide is made by reduction of nitric acid, by treating copper with nitric acid. It combines directly with oxygen, forming the strongly colored and disagreeable-smelling nitrogen peroxide.

Nitrogen peroxide gives up a part of its oxygen easily, and is hence a good oxidizing agent. It is thus reduced to nitric oxide, which in the air takes up oxygen.

## CHAPTER IX.

### CARBON.

WHEN most substances from the vegetable or animal kingdom are heated to a sufficiently high temperature they *blacken*, and afterwards, if heated in the air, they burn up, as we say. When we consider the great variety of substances found in living things, it is certainly remarkable that nearly all have this property in common. It is due to the fact that *nearly all animal and vegetable substances contain the element carbon*. When they are heated the other elements present are first driven off in various forms of combination, while the carbon is the last to go. If the heating is carried on in the air, the carbon finally combines with oxygen to form a colorless gas—it burns up. Carbon is the central element of organic nature. There is not a living thing, from the minutest microscopic animal to the mammoth, from the moss to the giant tree, which does not contain this element as an essential constituent. The number of the compounds which it forms is almost infinite, and they present such peculiarities that they are commonly treated under a separate head, “Organic Chemistry.” There is no good reason for this, except the large number of the compounds. The special study of these compounds can hardly be profitable to those who are in the earliest stages

of their work in chemistry, though, at the proper time, it forms an extremely valuable branch of study. For our present purpose it will suffice to consider the chemistry of the element itself, and of a few of its more important simple compounds.

**Occurrence.**—From what has already been said, it will be seen that the principal form in which carbon occurs in nature is in combination with other elements. It occurs not only in living things, but in their fossil remains, as in coal. Coal-oil, or petroleum, the formation of which was in some way connected with the processes involved in the formation of coal, consists of a large number of compounds which contain only carbon and hydrogen. Most products of plant-life contain the elements carbon, hydrogen, and oxygen. Among the more common of these products may be mentioned sugar, starch, cellulose, the fats, etc. Most products of animal life contain carbon, hydrogen, oxygen, and nitrogen. Among them may be mentioned albumin, fibrin, casein, etc. Carbon occurs in the atmosphere in the form of carbon dioxide. [What evidence have we had showing the presence of carbon dioxide in the air?] It also occurs in the form of salts of carbonic acid; the carbonates, which are widely distributed, forming whole mountain-ranges. Limestone, marble, and chalk are calcium carbonate.

Uncombined, the element occurs pure in two very different forms in nature: (1) As *diamond*; and (2) as *graphite*, or *plumbago*.

Before considering the evidence which leads to the conclusion that diamond and graphite are only modifications of the same element, and that while closely related to each other they are also equally closely related to charcoal, it

will be best to study separately the properties of each of these three substances.

**1. Diamond.**—The diamond is found in but few places on the earth. Practically nothing is known as to the conditions which gave rise to its formation. The celebrated diamond-beds are in the East Indies, Borneo, Sumatra, Brazil, Australia, Mexico, and at the Cape of Good Hope. When found, diamonds are covered with an untransparent layer, which must be removed before the beautiful properties are apparent. The crystals are sometimes what are known as octahedrons; that is to say, they are regular eight-sided figures, though usually they are somewhat more complicated. It is the hardest substance known.

If heated to a very high temperature without access of air, it swells up and is converted into a black mass resembling graphite. This change takes place without loss in weight. Heated to a high temperature in oxygen, it burns up, yielding only carbon dioxide. It is insoluble in all known liquids.

**2. Graphite.**—Graphite, or plumbago, is found in nature in large quantities. Sometimes it is crystallized, but in forms entirely different from those assumed by the diamond. It can be prepared artificially by dissolving charcoal in molten iron, from which solution, on cooling, it is deposited as graphite. It has a grayish-black color and a metallic lustre. It is quite soft, leaving a leaden-gray mark on paper when drawn across it, and is hence used in the manufacture of so-called *lead* pencils. It is sometimes called black-lead.

When heated without access of air it remains unchanged. Heated to a very high temperature in the air, or in oxygen,

it burns up, forming only carbon dioxide. Like the diamond, it is insoluble in all known liquids.

**3. Amorphous Carbon.**—All forms of carbon which are not diamond, nor graphite, are included under the name *amorphous carbon*. The name signifies simply that it is not crystallized. The most common form of amorphous carbon is ordinary charcoal.

Charcoal is that form of carbon which is made by the *charring process*, which consists simply in heating without a free supply of air to effect complete combustion. The substance almost exclusively used in the manufacture of charcoal is wood. As has already been stated, wood is made of a large number of substances, nearly all of which, however, consist of the three elements carbon, hydrogen, and oxygen. One of the chief constituents of all kinds of wood is cellulose. Now, when we set fire to a piece of wood,—that is to say, when we heat it up to the temperature at which oxygen begins to act on it,—it burns, if air is present. The chemical changes which take place are complex under ordinary circumstances; but if care be taken, the combustion can be made complete, when all the carbon is converted into carbon dioxide, and all the hydrogen into water. If, on the other hand, the air be prevented from coming in contact with the wood in sufficient quantity to effect complete combustion, the hydrogen is given off partly as water and partly in the form of volatile compounds containing carbon and oxygen. The carbon, however, is mainly left behind as charcoal, as there is not enough oxygen to convert it into carbon dioxide.

The above statements will enable the student to understand the working of a charcoal-kiln. This consists essentially of a pile of wood so arranged as to leave spaces be-

tween the pieces. The pile is covered with some rough material through which the air will not pass easily, as, for example, a mixture of powdered charcoal, turf, and earth. Small openings are left in this covering so that after it is kindled the wood will continue to burn slowly. The changes above mentioned take place, the gases or volatile substances passing out of the top of the kiln, and appearing as a thick smoke. In due time the holes through which the air gains access to the wood, and which also make the burning possible, are stopped up, and the burning stops. Charcoal, which is impure amorphous carbon, is left behind. As wood always contains some incombustible substances in small quantity, these are, of course, found in the charcoal. When the wood or charcoal is burned, these substances remain behind as the ash.

Ordinary charcoal is a black, comparatively soft substance. It burns in the air, though not easily, unless the gases which are formed are constantly removed and fresh air is supplied,—conditions which are met by a good draught, or by blowing upon the fire with a bellows. It burns readily in oxygen, as we have seen (Experiment 22). The product of the combustion in oxygen and in air, when the conditions are favorable, is carbon dioxide,  $\text{CO}_2$ . In the air, when the draught is bad, another compound of carbon and oxygen, carbon monoxide,  $\text{CO}$ , is formed. Heated without access of air, charcoal remains unchanged. Charcoal is insoluble in all known liquids.

Besides wood charcoal, there are other forms of amorphous carbon, which are manufactured for special purposes, or are formed in processes carried on for the sake of other products. *Coke* is a form of amorphous carbon which is made by heating ordinary gas coal without access of air, as is

done on a large scale in the manufacture of illuminating gas. Coke bears to coal about the same relation that charcoal bears to wood.

**Lamp-black** is a very finely divided form of charcoal which is deposited on cold objects placed in the flames of burning oils. The oils consist almost exclusively of carbon and hydrogen. When burned in the air they yield carbon dioxide and water. If the flame be cooled down by any means, or if the supply of air be partly cut off, the carbon is not completely burned; the flame "smokes," as we say, and deposits soot. This soot is largely made up of fine particles of carbon. It is used in the manufacture of printer's-ink. Carbon is acted upon directly by very few substances, and is not soluble, so that it is impossible to destroy the color of printer's-ink without destroying the material upon which it is impressed.

**Bone-black, or Animal Charcoal**, is a form of amorphous carbon which is made by charring bones. Unless treated with an acid it contains the incombustible substances contained in bone, as calcium phosphate, etc.

Bone-black and wood-charcoal are very porous and have the power to absorb gases. When placed in air containing bad-smelling gases, these are absorbed and the air thus purified. When water which contains disagreeable substances is treated with charcoal, these are wholly or partly absorbed and the water improved. Charcoal-filters are therefore extensively used. A charcoal-filter to be efficient should be of good size, and from time to time the charcoal should be taken out and renewed. The small filters which are screwed into faucets are of little value, as the charcoal soon becomes charged with any objectionable material which may be present in the water.

Some coloring matters may be removed from liquids by passing the liquids through *bone-black filters*. On the large scale, this fact is taken advantage of in the refining of sugar. The solution of sugar first obtained from the cane or beet is highly colored; and if it were evaporated, the sugar deposited from it would be dark-colored. If, however, the solution be first passed through bone-black filters, the color is removed, and now, on evaporating, white sugar is deposited. In the laboratory constant use is made of this method for the purpose of purifying liquids.

**EXPERIMENT 86a.**—Make a filter of bone-black by fitting a paper filter into a funnel 12 to 15 mm. (5 to 6 inches) in diameter at its mouth. Half-fill this with bone-black. Make a dilute solution of indigo. Pour it through the filter. If the conditions are right the solution will pass through colorless.—Do the same thing with a dilute solution of litmus.—If the color is not completely removed by one filtering, filter it again.—The color may also be removed from solutions by putting some bone-black into them and boiling for a time.—Try this with half a litre each of the litmus and indigo solutions used in the first part of the experiment. Use about 4 to 5 grams bone-black in each case. Shake the solution frequently while heating.

Charcoal does not undergo decay in the air or under water nearly as readily as wood. That is another way of stating the chemical fact that the substances of which wood are made up are more susceptible to the action of other chemical substances than charcoal is. We have one illustration of this, indeed, in the relative ease with which charcoal and wood burn in the air. Piles which are driven below the surface of water are charred to protect them from the action of those substances which cause decay.

**Coal.**—Under this head are included a great many kinds of impure amorphous carbon which occur ready-formed in nature. Although we might distinguish between an almost infinite number of kinds of coal, for ordinary purposes they are separated into *hard* and *soft coals*, or *anthracite* and *bituminous coals*. Then there are substances more nearly allied to wood called *lignite*, and those which represent a very early stage in the process of coal-formation, viz., *peat*.

A close examination of all these varieties has shown that they have been formed by the gradual decomposition of vegetable material in an insufficient supply of air. The process has been going on for ages. Sometimes the substances have, at the same time, been subjected to great pressure, as can be seen from the position in which they occur in the earth. The products in the earlier stages of the coal-forming process would be more closely allied to wood than those formed in the later stages.

All forms of coal contain other substances in addition to the carbon. The soft coals are particularly rich in other substances. When heated they give off a mixture of gases and the vapors of volatile liquids. The gases are, for the most part, useful for illuminating purposes. The liquids form a black, tarry mass known as *coal-tar*, from which are obtained many valuable compounds of carbon. The gases are passed through water for the purpose of removing certain impurities. This water absorbs ammonia and forms the *ammoniacal liquor* of the gas-works, which, as has been stated, is the principal source of ammonia.

**Diamond, Graphite, and Charcoal Different Forms of the Element Carbon.**—According to what we learned in the first chapter, an element is a form of matter which cannot be decomposed into simpler forms by any means now known

to chemists. From hydrogen we can get nothing but hydrogen, except by bringing it together with some other element; from nitrogen we can get nothing but nitrogen, etc. In the case of carbon, however, it is possible for the element to appear in three forms, which differ markedly from one another. It is difficult to conceive that the soft, black charcoal and the dull, gray, soft graphite are chemically identical with the hard, transparent, brilliant diamond. Yet this is undoubtedly the case, as can be proved by a very simple experiment. Each of the substances when burned in oxygen yields carbon dioxide. Now, the composition of carbon dioxide is known, so that if we know the weight of carbon dioxide formed in any given case, we know also the weight of carbon contained in it. If we burn the same weights of diamond, of graphite, and of charcoal, we find that the same quantity of carbon dioxide is formed in each case, and in each case the weight of the carbon contained in the carbon dioxide formed is equal to the weight of substance burned.

[PROBLEM.—How much carbon dioxide,  $\text{CO}_2$ , should be obtained by burning 0.5 gram diamond? The combining weight of carbon is 12.]

Notwithstanding the marked differences in their appearance, the three forms of carbon have, as we have seen, some properties in common. They are insoluble in all known liquids. They are tasteless and inodorous. They are infusible. When heated without access of air, they remain unchanged, unless the temperature is very high.

That one and the same substance can appear in markedly different forms under different conditions is seen in the case of water. Hail and snow would hardly be suspected

of being the same substance by one who was not quite familiar with them. The difference in this case, as in that which we have been considering, is believed to be due to the way in which the small particles of which the substances are made up are arranged with reference to one another. If we had a number of small pieces of wood all of the same size and shape, say cubical, and should carefully arrange these in some regular way, we might easily make a comparatively compact mass of them, and the mass would have a regular form. We might arrange them, further, in a second way with regularity. And we might simply throw the pieces together in a jumble. These three kinds of arrangement would represent, in a rough way, the difference between the three forms of carbon. Each pile would be made of wood, but still in outward appearance they would differ from one another.

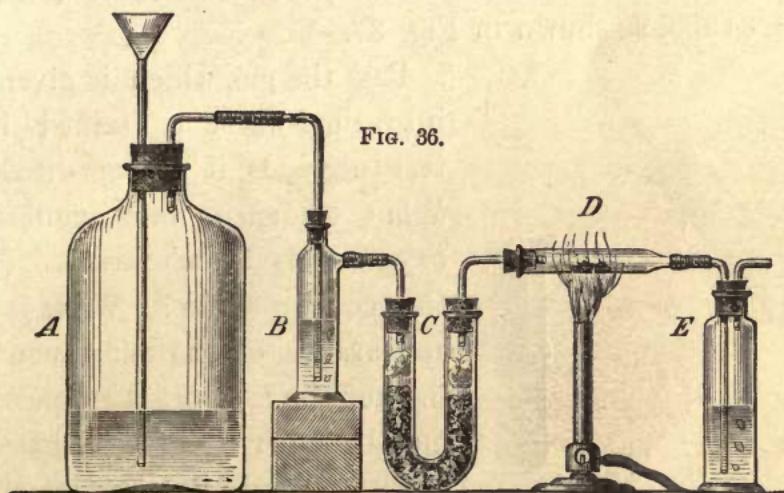
**Chemical Conduct of Carbon.**—At ordinary temperatures carbon is an inactive element. If it be left in contact with any one of the elements thus far considered,—viz., hydrogen, oxygen, chlorine, and nitrogen,—no change takes place. Indeed, unless the temperature be raised it will not combine with any other elements. At higher temperatures, however, it has marked affinity for other elements, especially for oxygen. Under proper conditions it combines also with nitrogen, with hydrogen, and with many other elements. It combines with oxygen either directly, as when it burns in the air or in oxygen; or it abstracts oxygen from some of the oxides.

The direct combination of carbon and oxygen has already been shown in Experiment 22, and is familiar to every one in the fire in a charcoal furnace. That carbon dioxide is the product may be shown by passing the gas

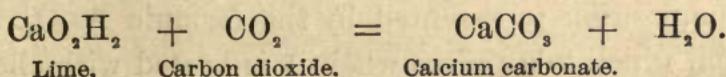
into lime-water or baryta-water, when insoluble calcium, or barium carbonate, will be thrown down.

**EXPERIMENT 87.**—Put a small piece of charcoal in a piece of hard glass tube. Pass oxygen through the tube, at the same time heating it. Pass the gases into clear lime-water. Arrange the apparatus as shown in Fig. 36.

FIG. 36.



*A* is a large bottle containing oxygen; *B* is a cylinder containing sulphuric acid; *C* is a U-tube containing calcium chloride; *D* is the hard glass tube containing the charcoal; *E* is the cylinder with clear lime-water. In what previous experiment was this method of showing the formation of carbon dioxide used? The reason why it is used is simply that an insoluble compound is formed, and this can be seen, and it can be separated from the liquid and examined. The reaction which takes place is represented thus:



No other common gas acts in this way on lime-water. Hence, when, under ordinary circumstances, a gas is passed

into lime-water and an insoluble substance is formed, we may conclude that the gas is carbon dioxide.

The abstraction of oxygen from compounds by means of carbon may be illustrated in a number of ways.

**EXPERIMENT 88.**—Mix together 2 or 3 grams powdered copper oxide, CuO, and about one tenth its weight of powdered charcoal; heat in a tube to which is fitted an outlet tube, as shown in Fig. 37.

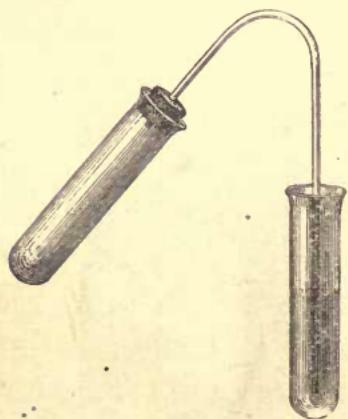
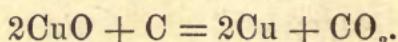


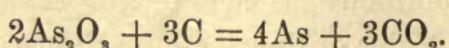
FIG. 37.

Pass the gas which is given off into lime-water contained in a test-tube. Is it carbon dioxide? What evidence have you that oxygen has been extracted from the copper oxide? What is the appearance of the substance left in the tube? Does it suggest the metal copper? Treat a little of it with strong nitric acid. What

should take place if the substance is metallic copper? (See Experiment 79.) What does take place? The reaction between the charcoal and the copper oxide is represented thus:



**EXPERIMENT 89.**—Perform a similar experiment with a little *white arsenic* in a small glass tube closed at one end. Take about equal parts of charcoal and arsenic. White arsenic is a compound of the element arsenic and oxygen, of the composition represented by the formula As<sub>2</sub>O<sub>3</sub>. The reaction which takes place when it is heated with charcoal is represented thus:



The element arsenic formed is volatile, and is hence driven out of the bottom of the tube and deposited on the walls above the mixture in the form of a mirror with a metallic lustre.

The abstraction of oxygen from a compound is known as *reduction*, as has already been explained. Hence carbon is called a reducing agent. It is indeed the reducing agent which is most extensively used in the arts. Its chief use is in extracting metals from the ores, which are the forms in which they occur in nature. Thus, iron does not occur in nature as iron, but in combination with other elements, especially with oxygen. In order to get the metal, the ore must be reduced, or, in other words, the oxygen must be extracted. This is invariably accomplished by heating it with some form of carbon, either charcoal or coke.

[What other element already considered acts as a reducing agent? Give an example of its reducing power.]

The elements thus far considered, with the exception of carbon, are gases. Carbon is not known in the form of gas. It cannot even be melted. In comparing the weights of equal volumes of the gaseous elements it will be found, as has been found in the case of hydrogen, chlorine, oxygen, and nitrogen, that they bear to one another the same relations as the combining weights. Whether this rule holds good in regard to carbon, we cannot say.

## CHAPTER X.

### COMPOUNDS OF CARBON WITH HYDROGEN, WITH OXYGEN, AND WITH NITROGEN.

IN the laboratory it is not a simple matter to effect combination between carbon and hydrogen except in a few simple cases. In nature processes are in operation which give rise to the formation of a large number of compounds containing these elements; and, further, in one branch of manufacture, the preparation of illuminating gas from coal, the conditions are such as to cause the combination of carbon and hydrogen, several interesting compounds being thus formed. There are no other two elements which combine with each other in as many different proportions as carbon and hydrogen. The compounds thus formed are known as *hydrocarbons*. The number of hydrocarbons known is very great, being somewhere between one and two hundred. Fortunately, investigation has shown that quite simple relations exist between these compounds ; and hence, though the number is large, the study is not as difficult as might be expected.

**Petroleum** is an oily liquid found in many places in the earth in large quantity. Its formation is in some way connected with the formation of coal. In the earth it contains both gases and liquids. When it is brought into the air, the pressure being removed, the gases are given off. There

are several gases given off, and a large number of liquids left behind. The simplest gas corresponds to the formula  $\text{CH}_4$ , the next to  $\text{C}_2\text{H}_6$ , the next to  $\text{C}_3\text{H}_8$ , the next to  $\text{C}_4\text{H}_{10}$ . An examination of the liquid has shown it to contain other hydrocarbons of the formulas  $\text{C}_5\text{H}_{12}$ ,  $\text{C}_6\text{H}_{14}$ ,  $\text{C}_7\text{H}_{16}$ ,  $\text{C}_8\text{H}_{18}$ , etc. It will be seen that these compounds bear a simple relation to one another, as far as composition is concerned. Arranging them in a perpendicular series we have

- $\text{CH}_4$ , Methane, or Marsh gas;
- $\text{C}_2\text{H}_6$ , Ethane;
- $\text{C}_3\text{H}_8$ , Propane;
- $\text{C}_4\text{H}_{10}$ , Butane;
- $\text{C}_5\text{H}_{12}$ , Pentane;
- $\text{C}_6\text{H}_{14}$ , Hexane;
- $\text{C}_7\text{H}_{16}$ , Heptane;
- $\text{C}_8\text{H}_{18}$ , Octane.

The first member of the series differs from the second by  $\text{CH}_2$ ; there is also this same difference between the second and third, the third and fourth, and, in general, between any two consecutive members in the series. This relation is known as *homology*, and such a series is known as an *homologous series*. Carbon is distinguished from all other elements by its power to form homologous series.

Besides the series above mentioned, which, as its simplest member is marsh gas,  $\text{CH}_4$ , is known as the *marsh-gas series*, there are other homologous series of hydrocarbons. There is one beginning with ethylene,  $\text{C}_2\text{H}_4$ , examples of which are

- Ethylene,  $\text{C}_2\text{H}_4$ ;
- Propylene,  $\text{C}_3\text{H}_6$ ;
- Butylene,  $\text{C}_4\text{H}_8$ .

There is another beginning with acetylene,  $C_2H_2$ , examples of which are

Acetylene,  $C_2H_2$ ;

Allylene,  $C_3H_4$ .

Another series begins with benzene,  $C_6H_6$ . Some of the members of this series are

Benzene,  $C_6H_6$ ;

Toluene,  $C_7H_8$ ;

Xylene,  $C_8H_{10}$ .

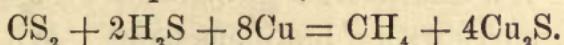
These are the hydrocarbons which are obtained from coal-tar.

The hydrocarbons are capable of undergoing a great variety of changes, and thus yielding a great many different products. Among the products thus obtained from the hydrocarbons and closely related to them are compounds known as alcohols, ethers, acids, aldehydes, etc. As examples of alcohols, *wood-spirit*, or *methyl alcohol*,  $CH_3O$ , and *spirits of wine*, or *ethyl alcohol*,  $C_2H_5O$ , may be mentioned. *Ordinary ether*, or *ethyl ether*,  $C_4H_{10}O$ , is the best-known example of the class of compounds called ethers. *Formic acid* obtained from ants, *acetic acid*, the acid of vinegar, *oxalic acid*, and *tartaric acid* are examples of the acids.

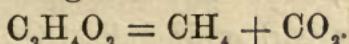
The study of these substances is simple enough; but as the relations between the compounds of carbon are not met with to any extent between the compounds of other elements, the interest connected with them is rather of a special character, and it is therefore better to leave their consideration until after a general survey of the field of chemistry has been made. The best reason for this course is, perhaps, that the study of the compounds of the other elements is a better preparation for the more special study

of the compounds of carbon than the study of the compounds of carbon for the study of other compounds. For the purpose for which this book is designed it appears more profitable, therefore, to confine our attention here to a few of the simplest compounds of carbon.

**Marsh Gas, Methane, Fire-Damp, CH<sub>4</sub>.**—Marsh gas is found in nature in petroleum, and is given off when the oil is taken out of the earth and the pressure is removed. It is formed, as the name implies, in marshes, as the product of a reducing process. Vegetable matter is composed of carbon, hydrogen, and oxygen. When it undergoes decomposition in the air in a free supply of oxygen, the final products formed are carbon dioxide and water. When the decomposition takes place without access of oxygen, as under water, marsh gas, which is a reduction product, is formed. The gas can be made in the laboratory by passing a mixture of hydrogen sulphide, H<sub>2</sub>S, and the vapor of carbon bisulphide, CS<sub>2</sub>, over heated copper. The sulphur is extracted from the compounds, and the carbon and hydrogen combine, as represented in the equation



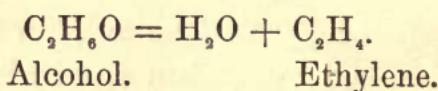
Marsh gas is met with in coal-mines, and is known to the miners as *fire-damp*, damp being the general name applied to a gas, and the name fire-damp meaning a gas that burns. To prepare it in the laboratory, it is most convenient to heat a mixture of sodium acetate and quick-lime. The change which takes place will be most readily understood by considering it as a simple decomposition of acetic acid. Acetic acid has the formula C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>. When heated alone, it boils and does not suffer decomposition. If it be converted into a salt, and heated in the presence of a base, it breaks up into marsh gas and carbon dioxide:



The carbon dioxide, which with bases forms salts, does not pass off, but remains behind in the form of a salt of carbonic acid.

Marsh gas is a colorless, transparent, tasteless, inodorous gas. It is slightly soluble in water. It burns, forming carbon dioxide and water. When mixed with air, the mixture explodes if a flame or spark comes in contact with it. This is one of the causes of the explosions which so frequently occur in coal-mines. To prevent these explosions a special lamp was invented by Sir Humphrey Davy, which is known as *Davy's safety-lamp*. The simple principles involved in its construction will be explained when the subject of *flame* is considered.

**Ethylene, Olefiant Gas,  $C_2H_4$ .** — This hydrocarbon is formed by heating a mixture of ordinary alcohol and concentrated sulphuric acid. The reaction is represented thus :



Ethylene is a colorless gas, which can be condensed to a liquid. It burns with a luminous flame. With oxygen it forms an explosive mixture.

**Acetylene,  $C_2H_2$ .** — Acetylene is formed when a current of hydrogen is passed between carbon poles, which are incandescent in consequence of the passage of a powerful electric current. In this case carbon and hydrogen combine directly. It is formed also when the flame of an ordinary laboratory gas-burner (Bunsen burner) "strikes back," or burns at the base without a free supply of air. Its odor is unpleasant. It burns with a luminous, smoky flame.

**Carbon Dioxide,  $CO_2$ .** — The principal compound of carbon and oxygen is carbon dioxide,  $CO_2$ , commonly known

as *carbonic-acid gas*. Under the head of The Atmosphere attention was called to the fact that this gas is a constant constituent of the air, though its relative quantity is small. It issues from the earth in many places, particularly in the neighborhood of volcanoes. Many mineral waters contain it in large quantity, as the waters of Pyrmont, Selters, and the Geyser Spring at Saratoga. In small quantity it is present in all natural waters. In combination with bases it occurs in enormous quantities, particularly in the form of calcium carbonate,  $\text{CaCO}_3$ , varieties of which are ordinary limestone, chalk, marble, and calc-spar. Dolomite, which forms mountain-ranges, being particularly abundant in the Swiss Alps, is a compound containing calcium carbonate and magnesium carbonate,  $\text{MgCO}_3$ .

Carbon dioxide is constantly formed in many natural processes. Thus, all animals that breathe in the air give off carbon dioxide from their lungs.

**EXPERIMENT 90.**—Force the gases from the lungs through some lime-water by means of an apparatus arranged as shown in Fig. 38. A white, insoluble compound is formed. This is calcium carbonate. On addition of a few drops of hydrochloric acid it dissolves.

That carbon dioxide is formed in the combustion of charcoal and wood has already been shown. In a similar way it can be shown that the gas is formed whenever any of our ordinary combustible materials are burned. From our fires, as from our lungs, and from the lungs of all animals, then,



FIG. 38.

carbon dioxide is constantly given off. Further, the natural processes of decay of both vegetable and animal matter tend to convert the carbon of this matter into carbon dioxide, which is then spread through the air. The process of alcoholic fermentation, and some other like processes, also give rise to the formation of carbon dioxide. In all fruit-juices there is contained sugar. When the fruits ripen, fall off, and undergo spontaneous change, the sugar is changed to alcohol and carbon dioxide.

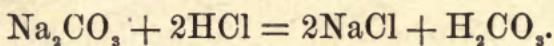
We see, thus, that there are many important sources of supply of carbon dioxide, and we can readily understand why the gas should be found everywhere in the air.

**Preparation of Carbon Dioxide.**—The easiest way to get carbon dioxide unmixed with other substances is to add an acid to a carbonate. Whenever any acid is added to any carbonate there is an evolution of gas.

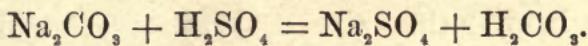
**EXPERIMENT 91.**—In test-tubes add successively dilute hydrochloric, sulphuric, nitric, and acetic acids to a little sodium carbonate. In each case pass the gas given off through lime-water; and insert a burning stick in the upper part of each tube.—Perform the same experiment with small pieces of marble.

In the decomposition of the carbonates or salts of carbonic acid by other acids, we see exemplified the same principle as that which is made use of in setting nitric acid free from a nitrate, or hydrochloric acid from sodium chloride, by means of sulphuric acid. The strong acid appropriates the metal and gives up its hydrogen. As carbonic acid is the weakest acid, it is set free from its salts by any other acid. When any acid, say hydrochloric acid, is added to a carbonate, say sodium carbonate, the first action consists in an

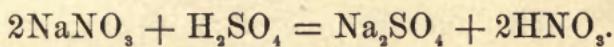
exchange of the hydrogen of the acid for the metal of the carbonate:



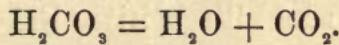
If sulphuric acid be used, the reaction is represented thus:



This reaction is analogous to that which takes place between sodium nitrate and sulphuric acid in the preparation of nitric acid:



Carbonic acid, however, is an unstable substance, and breaks up into water and carbon dioxide as soon as it is liberated from its salts:

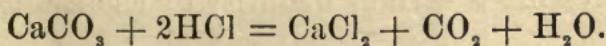


Hence, whenever a carbonate is treated with an acid, carbon dioxide is evolved.

It will be seen that the decomposition of carbonic acid into carbon dioxide and water is analogous to the decomposition of nitrous acid,  $\text{HNO}_2$ , into nitrogen trioxide and water; and similar to the decomposition of ammonium hydroxide into ammonia and water.

[What is a compound called which bears to an acid the relation which carbon dioxide bears to carbonic acid?]

For the purpose of preparing carbon dioxide in the laboratory, calcium carbonate in the form of marble, or limestone, and hydrochloric acid are commonly used. The reaction involved is represented thus:



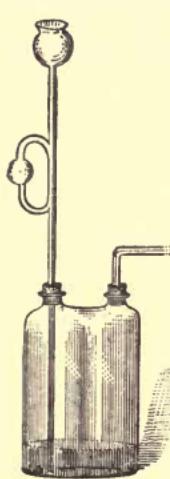


FIG. 39. **EXPERIMENT 92.**—Arrange an apparatus as shown in Fig. 39. In the flask put some pieces of marble, or lime-stone, and pour ordinary hydrochloric acid on it. The gas should be collected by displacement of air, the vessel being placed with the mouth upward, as the gas is much heavier than air. Collect several cylinders or bottles full of the gas. Into one introduce successively a lighted candle, a burning stick, a bit of burning phosphorus. They are all extinguished. Into another put a live mouse. With another proceed as if pouring water from

it. Pour the invisible gas upon the flame of a burning candle. Pour some of the gas from one vessel to another, and show that it has been transferred. Balance a beaker on a good-sized scales, and pour carbon dioxide into it. If the balance is at all sensitive, the pan on which the beaker is placed will go down.

Carbon dioxide is a colorless gas at ordinary temperature. When subjected to a low temperature and high pressure it is converted into a liquid; and when some of the liquid is exposed to the air, evaporation takes place so rapidly that a great deal of heat is absorbed, and some of the liquid becomes solid. The gas has a slightly acid taste and smell. It is not combustible, nor does it support combustion. It is not combustible for the same reason that water is not; because it already holds in combination all the oxygen it has the power to combine with. Before it can burn again, it must first be decomposed. Carbon has the power to combine with oxygen, and in so doing it gives rise to the formation of a definite quantity of heat. A kilogram of carbon represents a certain quantity of energy, which we

can get first in the form of heat and then convert into other forms, as electricity, motion, etc. After the kilogram of carbon has been burned, it no longer represents the energy it did in the form of carbon. A body of water elevated ten or fifteen feet represents a certain quantity of energy which can be obtained by allowing the water to fall upon the paddles of a water-wheel connected with the machinery of a mill. After the water has fallen, however, it no longer has power to do work, or it has no energy. In order that it may again do work, it must again be lifted. Not only does carbon dioxide not burn, but it does not support combustion. Although it contains a large quantity of oxygen in combination, it does not as a rule give it up to other substances.

[What gas containing oxygen in combination with another element does support combustion?]

Carbon dioxide is much heavier than air, its specific gravity being 1.529. A litre of the gas under standard conditions of temperature and pressure weighs 1.877 grams. It dissolves in water, one volume of water dissolving about one volume of the gas at the ordinary temperature. As is the case with all gases when the pressure is increased, the water dissolves more gas; and when the pressure is removed, the gas again escapes. The so-called "soda-water" is simply water charged with carbon dioxide under pressure. The escape of the gas, when the water is drawn, is familiar to every one. The carbon dioxide used in charging the water is generally made from a sodium salt of carbonic acid known as "bicarbonate of soda."

**Respiration.**—It was stated above that carbon dioxide is given off from the lungs just as it is from a fire, and the fact was demonstrated by means of a simple experiment.

It is a waste product of the processes going on in the animal body. Just as it cannot support combustion, so also it cannot support respiration. It is not poisonous any more than water is; but it is not able to supply the oxygen which is needed for breathing purposes, and hence animals die when placed in it. They die by suffocation, as they do in drowning. Any considerable increase in the quantity of carbon dioxide in the air above that which is normally present is objectionable, for the reason that it decreases the proportion of oxygen in the air which is breathed. If, however, pure carbon dioxide be introduced into the air, it has been found that as much as 5 per cent may be present without causing injury to those who breathe it. In a badly ventilated room in which a number of people are collected and lights are burning, it is well known that in a short time the air becomes foul, and bad effects, such as headache, drowsiness, etc., are produced on the occupants of the room. These effects have been shown to be due, not to the carbon dioxide, but to other waste products which are given off from the lungs in the process of breathing. The gases given off from the lungs consist of nitrogen, oxygen, carbon dioxide, and water vapor. Besides these, however, there are many substances in a fine state of division which contain carbon, and are in a state of decomposition. These are poisonous, and are the chief cause of the bad effects experienced in breathing air which has become contaminated by the exhalations from the lungs. As carbon dioxide is given off from the lungs at the same time, the quantity of this gas present is proportional to the quantity of the organic impurities. Hence, by determining the quantity of carbon dioxide we are enabled to form a judgment as to whether the air of a room occupied by human beings is fit for use

or not. As carbon dioxide is formed in the earth wherever an acid solution comes in contact with a carbonate, the gas is frequently given off from fissures in the earth. It is hence not unfrequently found in old wells which have not been in use for some time, and deaths have been caused by descending these wells for the purpose of repairing them. The gas is also frequently met with in mines, and is called *choke-damp* by the miners. The miners are aware that after an explosion caused by fire-damp there is danger of death from choke-damp. The reason is simple. When fire-damp, or marsh gas, explodes with air the carbon is converted into choke-damp, or carbon dioxide, and the hydrogen into water. Air in which a candle will not burn is not fit for breathing purposes.

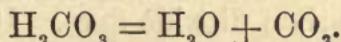
The rôle played by carbon dioxide in nature is extremely important and interesting. The carbon of living things is obtained from carbon dioxide, and returns to this form when life ceases. We have learned that all living things contain carbon as an essential constituent. Whence comes this carbon? Animals eat either the products of plant-life or other animals which derive their sustenance from the vegetable kingdom. The food of animals comes, then, either directly or indirectly from plants. But plants derive their sustenance largely from the carbon dioxide of the air. The plants have the power to decompose the gas with the aid of the direct light of the sun, and they then build up the complex compounds of carbon which form their tissues, using for this purpose the carbon of the carbon dioxide which they have decomposed. Many of these compounds are fit for food for animals; that is to say, they are of such composition that the forces at work in the animal body are capable of transforming them into animal tissues, or of oxidizing them, and

thus keeping the temperature of the body up to the necessary point. That part of the food which undergoes oxidation in the body plays the same part as fuel in a stove. It is burned up with an evolution of heat, the carbon being converted into carbon dioxide, which is given off from the lungs. From fires and from living animals carbon dioxide is returned to the air, where it again serves as food for the plants. When the life-process stops in the animal or plant, decomposition begins; and the final result of this, under ordinary circumstances, is the conversion of the carbon into carbon dioxide.

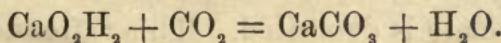
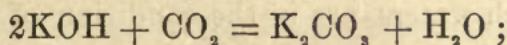
We see, thus, that under the influence of life and sunlight carbon dioxide is converted in the plant into compounds containing carbon which are stored up in the plant. These compounds are capable of burning, and thus giving heat; or some of them may be used as food for animals, assuming still more complex forms under the influence of the life-process of the animals. As long as life continues, plants and animals are storehouses of energy. When death occurs, the carbon compounds pass back to the form of carbon dioxide; the energy which was stored up is lost. The power to do work which the carbon compounds of plants and animals possess comes from the heat of the sun. It takes a certain quantity of this heat, operating under proper conditions, to decompose a certain quantity of carbon dioxide and elaborate the compounds contained in the plants. When these compounds are burned they give out the heat which was used up in their formation during the growth of the plants. These compounds are said to possess chemical energy. This has its origin in heat, and is capable of re-conversion into heat. The transformation of the energy of the sun's heat into chemical energy lies at the foundation

of all life. As the heat of the sun acting upon the great bodies of water and on the air gives rise to the movements of water which are so essential to the existence of the world as it is, so the action of the sun's rays on carbon dioxide, in the presence of the delicate and inexplicable mechanism of the leaf of the plant, gives rise to those changes in the forms of combination of the element carbon which accompany the wonderful process of life.

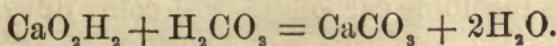
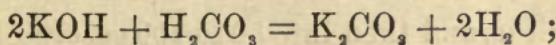
**Carbonic Acid and Carbonates.**—When carbon dioxide is passed into water the solution has a slightly acid reaction. [Try it.] The solution will act upon basic solutions and form salts. The formula of the sodium salt formed in this way has been shown to be  $\text{Na}_2\text{CO}_3$ ; that of the potassium salt,  $\text{K}_2\text{CO}_3$ , etc. These salts are plainly derived from an acid,  $\text{H}_2\text{CO}_3$ , which is carbonic acid. It is probable that this acid is contained in the solution of carbon dioxide in water. It is, however, so unstable that it breaks up into carbon dioxide and water :



When carbon dioxide acts upon a base it forms a salt. Thus, with potassium hydroxide or calcium hydroxide the action which takes place is represented thus :



With the acid the action would take place as represented thus :



**EXPERIMENT 93.**—Pass carbon dioxide into a solution of caustic potash until it will absorb no more. Add acid to some of this solution and convince yourself that the gas given off is carbon dioxide. Write the equations representing the reactions which take place on passing the carbon dioxide into the caustic potash solution, and on adding an acid to the solution. What evidence have you that the gas given off is carbon dioxide?

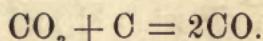
**EXPERIMENT 94.**—Pass carbon dioxide into 50 to 100 cc. clear lime-water. Filter off the white insoluble substance. Try the action of a little acid on it. What evidence have you that it is calcium carbonate? How could you easily distinguish between lime-water and a solution of caustic potash?

Although, as we have seen, when carbon dioxide is passed into lime-water calcium carbonate is thrown down, if we continue to pass the gas for some time the calcium carbonate dissolves, and finally the solution becomes clear. Water alone does not dissolve calcium carbonate, but water containing carbon dioxide does. If this solution be heated, the carbon dioxide is driven off and the calcium carbonate is again thrown down. Natural waters which flow over lime-stone take up more or less calcium carbonate by virtue of the carbon dioxide which they absorb from the air. Such waters are in the condition of the solution of calcium carbonate above referred to. When heated, the calcium carbonate is deposited. This is frequently noticed in the deposits in boilers and other vessels in which water is boiled.

**EXPERIMENT 95.**—Pass carbon dioxide first through a little water to wash it, and then into 50 to 100 cc. clear lime-water. At first the insoluble carbonate will come down, as in Ex-

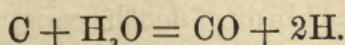
periment 94; but soon it will begin to dissolve, and finally an almost clear solution will be obtained. Heat this solution, and the insoluble carbonate will again appear.

✓ **Carbon Monoxide, CO.**—When a substance containing carbon burns in an insufficient supply of air,—as, for example, when the draught in a furnace is not strong enough to remove the products of combustion and supply fresh air,—the oxidation of the carbon is not complete, and the product, instead of being carbon dioxide, is carbon monoxide, CO. This substance can also be made by extracting oxygen from carbon dioxide. It is only necessary to pass the dioxide over heated carbon, when reaction takes place as represented thus :



This method of formation is illustrated in coal fires, and can be well observed in an open grate. The air has free access to the coal, and at the surface complete oxidation takes place. But that part of the carbon dioxide which is formed at the lower part of the grate is drawn up through the heated coal and is partly reduced to carbon monoxide. When the monoxide escapes from the upper part of the grate it again combines with oxygen, or burns, giving rise to the characteristic blue flame always noticed above a mass of burning coal. Should anything occur to prevent free access of air, carbon monoxide may easily escape complete oxidation.

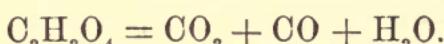
It is also formed by passing water over highly heated carbon, when this reaction takes place :



This is the reaction which is made use of in the manu-

facture of "water gas." The gas thus obtained is a mixture of hydrogen and carbon monoxide. Before use it is enriched by the addition of hydrocarbons from petroleum.

The easiest way to make carbon monoxide is to heat oxalic acid, which is a compound of carbon, hydrogen, and oxygen, of the formula  $C_2H_2O_4$ , with five to six times its weight of concentrated sulphuric acid. The change which takes place is represented thus :



Both carbon dioxide and monoxide are formed. Both are gases. In order to separate them the mixture is passed through a solution of caustic soda, which takes up the carbon dioxide [forming what?] and allows the monoxide to pass.

**EXPERIMENT 96.**—Put ten grams crystallized oxalic acid and 50-60 grams concentrated sulphuric acid in an appropriate-sized flask. Connect with two Wolff's flasks containing caustic-soda solution. Heat the contents of the flask gently. Collect some of the gas over water. Set fire to some, and notice the characteristic blue flame. Put a live mouse in a vessel containing a mixture of about equal parts of carbon monoxide and air. It will die unless removed.

Carbon monoxide is a colorless, tasteless, inodorous gas, insoluble in water. It burns with a pale blue flame, forming carbon dioxide. It is exceedingly poisonous when inhaled. Hence it is very important that it should not be allowed to escape into rooms occupied by human beings. We not unfrequently hear of deaths caused by the gases from coal stoves. The most dangerous of the gases given off from coal stoves is carbon monoxide. A pan of smoulder-

ing charcoal gives off this gas, and the poisonous character of the gas is well known, as it has been used to a considerable extent for the purpose of suicide, particularly in France.

At high temperatures carbon monoxide has a very strong affinity for oxygen, and is hence a good reducing agent. In the reduction of iron from its ores, the carbon monoxide formed in the blast-furnace plays an important part in the reducing process.

**EXPERIMENT 97.**—Pass carbon monoxide over some heated copper oxide contained in a hard glass tube. Is the oxide reduced? How do you know? Is carbon dioxide formed? What evidence have you? Was the carbon monoxide used free of carbon dioxide? If not, what evidence have you that carbon dioxide is formed in this experiment?

**Illumination, Flame, Blow-pipe, etc.**—As the substances used for illumination contain carbon, and the chemical processes involved consist largely in the oxidation of the carbon of these compounds, this is an appropriate place to consider briefly the subject of illumination, and also that of flame, and the blow-pipe, which is an extremely useful form of flame constantly used in the laboratory.

In all ordinary kinds of illumination we are dependent upon flames for the light. Whether we use illuminating gas, a lamp, or a candle, the light comes from a flame. In the first case, the gas is burned directly; in the case of the lamp, the oil is first drawn up the wick, then converted into a gas, and this burns; while, finally, in the case of the candle, the solid material of the candle is first melted, then drawn up the wick, converted into gas, and the gas burns, forming the flame. In each case we have, then, to

deal with a burning gas, and this burning gas we call a flame.

Most illuminating gas is made from coal by heating in closed retorts. As has already been explained, coal, particularly the softer kinds, contains compounds of carbon and hydrogen, together with some nitrogen and other elements. When it is heated the hydrogen passes off, partly in combination with carbon, as hydrocarbons, and partly in the free state. The nitrogen passes off as ammonia, and a large percentage of the carbon remains behind in the retort in the uncombined state as coke. The gases given off are purified, and form ordinary illuminating gas. One ton of coal yields on an average 10,000 cubic feet of gas. The value of a gas depends upon the quantity of light given by the burning of a definite quantity. It is measured by comparing it with the light given by a candle burning at a certain rate. The standard candle is one made of spermaceti, which burns at the rate of 120 grains per hour; that is to say, which, burning under ordinary conditions, loses 120 grains in one hour. The standard burner used for the gas is one through which 5 cubic feet of gas pass per hour. Now, if we wish to determine the illuminating power of a gas, we pass it through the standard burner at the rate mentioned, and compare the light which it gives with the light given by the standard candle. The comparison is easily made by means of a so-called *photometer*. The illuminating power of the gas is then stated in terms of candles. When we say that the illuminating power of a gas is fourteen candles, we mean that, when burning at the rate of 5 cubic feet per hour, its flame gives fourteen times as much light as the standard candle.

Ordinarily when we speak of a flame we mean a gas which is combining with oxygen. The hydrogen flame is simply the phenomenon accompanying the act of combination of the two gases hydrogen and oxygen. Owing to the fact that we are surrounded by oxygen, we speak of hydrogen as the burning gas. How would it be if we were surrounded by an atmosphere of hydrogen? Plainly, oxygen would then be a burning gas. If we cause a jet of oxygen to escape into a vessel containing hydrogen, a flame will appear where the oxygen escapes from the jet, if a light be applied. This is an experiment which requires great precautions, and, as the principle can be illustrated as well by means of illuminating gas, we may use this instead. Just as illuminating gas burns in an atmosphere of oxygen, so oxygen burns in an atmosphere of illuminating gas.

**EXPERIMENT 98.**—Break off the neck of a good-sized re-

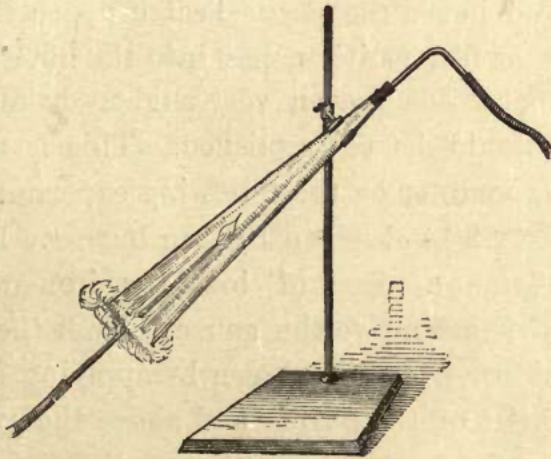


FIG. 40.

tort; fit a perforated cork to the small end; pass a piece of glass tube through the cork and connect by means of rubber hose with an outlet for gas. Fix the apparatus in

position, as shown in Fig. 40. Turn the gas on, and when the air is driven out of the retort-neck, light the gas. You now have the neck filled with illuminating gas, and the gas is burning at the mouth of the vessel. If now a platinum jet from which oxygen is issuing be passed up into the gas the oxygen will take fire, and a flame will appear where the oxygen escapes from the jet. The oxygen burns in the atmosphere of coal gas.

In considering the action of oxygen upon other substances, we learned that it is necessary that each of these substances should be raised to a certain temperature before it will combine with the oxygen. This statement is as true of gases as of other substances. When a current of hydrogen is allowed to escape into the air, or into oxygen, no action takes place unless it be heated up to its burning temperature, when it takes fire and continues to burn, as the burning of one part of the gas heats up the part which follows it, and hence the gas is heated up to the burning temperature as fast as it escapes into the air. If the gas should be cooled down even very slightly below this temperature, it would be extinguished. This is shown in a very striking manner by the following experiments :

**EXPERIMENT 99.**—Light a Bunsen burner. Bring down upon the flame a piece of brass or iron wire gauze. There is no flame above the gauze. That the gas passes through unburned can be shown by applying a light just above the outlet of the burner and above the gauze. The gas will take fire and burn. By simply passing through the thin wire gauze, then, the gas is cooled down below its burning temperature, and does not burn unless it is heated up again. Turn on a Bunsen burner. Do not light the gas. Hold a piece of wire gauze about one and a half to

two inches above the outlet. Apply a lighted match above the gauze, when the gas will burn above the gauze, but not below it. Here again the heat necessary to raise the temperature of the gas to the burning temperature cannot be communicated through the gauze. If in either of the above-described experiments the gauze be held in position for a time, it will probably become so highly heated that the gas on the side where there is no flame will be raised to the burning temperature. The instant that point is reached the flame becomes continuous.

The principle illustrated in the preceding experiments is utilized in the miner's *safety-lamp*, to which reference has already been made. One of the dangers which the coal-miner has to encounter is the occurrence of fire-damp, or methane,  $\text{CH}_4$ , which with air forms an explosive mixture. The explosion can only be brought about by contact of flame with the mixture. In order to avoid the contact, the flame of the safety-lamp is surrounded by wire gauze, as shown in Fig. 41. When a lamp of this kind is brought into an explosive mixture of marsh gas and air, what takes place? The mixture passes through the wire gauze and comes in contact with the flame, a small explosion inside the gauze occurs, but the flame of the burning gas inside the wire gauze cannot pass through and raise the temperature of the gas outside to the burning temperature. Hence no serious explosion can take place. The flickering of the flame of the

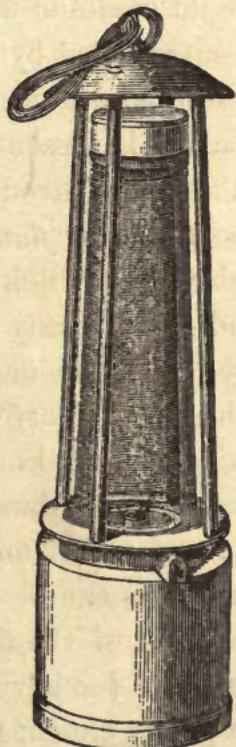


FIG. 41.

lamp, and the occurrence of small explosions inside, furnish the miner with the information that he is in a dangerous atmosphere.

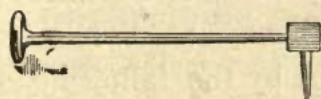
**Structure of Flames.**—The hydrogen flame consists of a thin envelope of burning hydrogen enclosing unburned gas, and surrounded by water vapor, which is the product of the combustion. The structure of other flames depends upon the complexity of the gases burned and the conditions under which the burning takes place. In general, a flame consists of an outer envelope of gas combining with oxygen, and hence hot, and an inner part which contains unburned gas, which is, for the most part, cool. A part of the unburned gas is, however, hot, and it would combine with oxygen were it not for the fact that it is surrounded by an envelope which prevents access of air. The *outer hot part* of the flame is called the *oxidizing flame*, because it presents conditions favorable to the oxidation of substances introduced into it. The *inner hot part* is called the *reducing flame*, because it consists of highly heated substances which have the power to combine with oxygen, and hence many compounds containing oxygen lose it, or are reduced, when introduced into this part of the flame. The hottest part of the flame is at the extreme top. Here oxidation is taking place most energetically. The hottest part of the unburned gases is at the tip of the dark central part of the flame. In the flame of a Bunsen burner the two parts can be distinguished very easily. The dark central part of the flame extends for some distance above the outlet of the burner. If the holes at the base of the burner be partly closed, the tip of the central part of the flame becomes luminous. This luminous tip is most efficient for the purpose of reduction. The principal parts of the flame

are those marked in Fig. 42. *B* is the central cone of unburned gas. *C* is the luminous tip, the best part of the flame for reduction. *A* is the envelope of burning gas. This is further surrounded by a non-luminous envelope consisting of the products of combustion, carbon dioxide and water vapor. Certain metals placed in the upper end of the flame take up oxygen, because they are highly heated in the presence of oxygen. Certain oxides lose their oxygen when placed in the tip of the central cone, because the gases are here heated to the temperature at which they have the power to combine with oxygen.



FIG. 42.

The oxidizing and reducing flames are frequently utilized in the laboratory. For the purpose of increasing their efficiency a *blow-pipe* is used. This is a tube through which air is blown by means of the mouth into a flame. It is usually constructed in the shape shown in Fig. 43. At the



smaller end, which is placed in the flame, there is usually a small tube of platinum. The blow-pipe may be used with the flame of a candle, an alcohol-lamp, or a gas-lamp. It is most frequently used with the gas-lamp. A piece of brass tubing which fits snugly in the tube of a Bunsen burner is cut off and hammered together so as to leave a narrow slit-like opening. This tube is then slipped into the burner, as shown in Fig. 44. It reaches to the bottom of the burner, and thus cuts off the supply of air which usually enters the holes at the base. The gas is now lighted and the current so regulated that there is a small flame about  $1\frac{1}{2}$  to 2 inches high. The tip of the blow-pipe is placed on the slit of the burner in

FIG. 43.

the flame, so that it extends about one third the way across it, as shown in Fig. 45. By blowing regularly and not too violently through the pipe the flame is forced down in the same direction as the end-piece of the blow-pipe, and the slant of the burner slit.

Under proper conditions it separates sharply into a central blue part and an outer part of another color. The direction and lines of division of the flame are

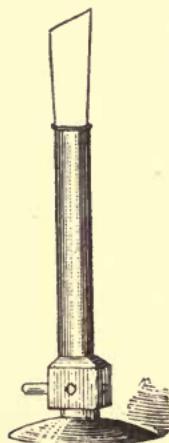


FIG. 44.



FIG. 45.

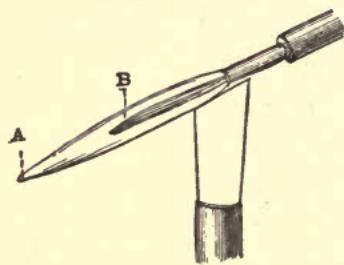


FIG. 46.

indicated in Fig. 46. The extreme outer tip *A* is the most efficient oxidizing flame. The tip *B* of the inner blue part is the most efficient reducing flame.

The use of the blow-pipe is illustrated by the following experiments:

**EXPERIMENT 100.**—Select a piece of charcoal about 4 inches long by 1 inch wide and 1 inch thick, with one surface plane.\* Near the end of the plane surface make a cavity by pressing the edge of a cent piece or similar coin against it, and turning it completely round a few times. Mix together equal small quantities of dry sodium carbonate and lead oxide. Put a little of the mixture in the cavity in the charcoal, and heat it in the reducing flame produced by the blow-pipe. In a short time globules of

\* Pieces of charcoal prepared for blow-pipe work can be bought from dealers in chemical apparatus at small cost.

metallic lead will be seen in the molten mass. After cooling, scrape the solidified substance out of the cavity in the charcoal. Put it in a small mortar, treat it with a little water, and, after breaking it up and allowing as much as possible to dissolve, pick out the metallic beads. [Is it malleable or brittle? Is metallic lead malleable or brittle? Is it dissolved by hydrochloric acid? Is lead soluble in hydrochloric acid? Is it soluble in nitric acid? Is lead soluble in nitric acid?] The action of the acids may be tried by putting the bead on a small dry watch-glass and adding a few drops of the acid. [Does the substance act like lead? What has become of the oxygen with which the lead was combined in the oxide? Is there any special advantage in having a support of charcoal for this experiment?]

**EXPERIMENT 101.**—Heat a small piece of metallic lead on charcoal in the oxidizing blow-pipe flame. Notice the formation of the oxide, which forms a coating or film on the charcoal in the neighborhood of the metal. [Is there any analogy between this process and the burning of hydrogen? In what does the analogy consist? What differences are there between the two processes?]

Some oxides are reduced very easily when heated in the reducing blow-pipe flame. Others are not. We are frequently able to judge of the composition of a substance by heating it in the blow-pipe flame and noticing its conduct. Some metals are easily oxidized in the oxidizing flame. Some form characteristic films of oxides on the charcoal, and in some cases it is possible to detect the presence of certain substances by noticing the color of the film of oxide. The blow-pipe is therefore of great value as affording a means of detecting the presence of certain elements in

mixtures or compounds of unknown composition. The chemical principles involved in its use will be clear from what has already been said.

**Causes of the Luminosity of Flames.**—It is evident from what we have seen that flames vary greatly in their light-giving power. The hydrogen flame, for example, gives practically no light. This is also the case with the flame of the Bunsen burner; while, on the other hand, the flame of illuminating gas burning under ordinary circumstances, and of a candle, etc., give light. What is the difference due to? There are several causes which operate to make a flame give light, and *vice versa*. In the first place, if a solid substance which does not burn up is introduced into a non-luminous flame, a part of the heat appears as light. This is seen when a spiral of platinum wire is introduced into a hydrogen flame. It has also been shown by introducing a piece of lime into the hot non-luminous flame of the oxyhydrogen blow-pipe. A similar cause operates in ordinary gas flames to make them luminous. There are always present particles of unburned carbon, as can be shown by putting a piece of porcelain or any solid substance into the flame, when there will be deposited in it a layer of soot, which consists mainly of finely divided carbon. In the flame these particles of carbon are heated to the temperature at which they give light. Again, it has been found that the same candle gives more light at the level of the sea than it does when at the top of a high mountain, as Mont Blanc, on which the experiment was actually performed. This is partly due to a difference in the density of the gases. Naturally, the denser the gas the more active the combustion, the greater the heat, and the greater the light. This last statement ceases to be true when the oxi-

dation becomes sufficient to burn up all the solid particles of carbon in the flame. If gases which in burning give light are cooled down before they are burned, the luminosity is diminished, and, conversely, non-luminous flames may be rendered luminous by heating the gases before burning them.

Gases which give luminous flames give non-luminous flames when diluted to a sufficient extent with neutral gases, such as nitrogen and carbon dioxide, which neither burn nor support combustion.

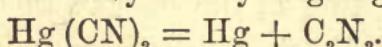
All the statements made in regard to the causes of the luminosity of flames are based upon carefully performed experiments. These experiments, however, cannot readily be repeated by the student in the laboratory in a satisfactory way. One constant reminder of the possibility of rendering a luminous flame non-luminous, and *vice versa*, is furnished by the burner universally used in chemical laboratories, and called, after the name of its inventor, the *Bunsen burner*. The construction of this burner is easily understood. It consists of a base and an upper tube. The base is connected by means of a rubber tube with the gas supply. The gas escapes from a small opening in the base, and passes up through the tube. At the lower part of the tube there are two holes, which may be opened or closed by turning a ring with two corresponding holes in it. When the gas is turned on, it is lighted at the top of the tube. Air is at the same time drawn through the holes at the base. The result is that the flame is practically non-luminous. If the ring at the base be turned so that the air-holes are closed, the flame becomes luminous. The advantage of the non-luminous flame for laboratory use con-

sists in the fact that it does not deposit soot, and, at the same time, gives a good heat.

[Could the hydrogen flame deposit soot?]

The non-luminosity of the flame of the Bunsen burner appears to be due to several causes : (1) Dilution of the gases by means of the nitrogen of the air; (2) Cooling of the gases by the entrance of the air; (3) Burning of the solid particles by the aid of the oxygen of the air admitted to the interior of the flame.

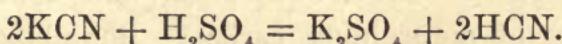
**Cyanogen,  $\text{C}_2\text{N}_2$ .**—Carbon does not combine with nitrogen under ordinary circumstances. If, however, they are brought together at very high temperatures in the presence of metals, they combine to form compounds known as *cyanides*. Thus, when nitrogen is passed over a highly heated mixture of carbon and potassium carbonate,  $\text{K}_2\text{CO}_3$ , the compound potassium cyanide,  $\text{KCN}$ , is formed. Carbon containing nitrogen, as animal charcoal, when ignited with potassium carbonate, reduces the potassium carbonate, forming potassium, which causes the carbon and nitrogen to combine, forming potassium cyanide. When refuse animal substances, such as blood, horns, claws, hair, wool, etc., are heated together with potassium carbonate and iron, a substance known as *potassium ferrocyanide*, or *yellow prussiate of potash*,  $4\text{KCN} \cdot \text{Fe}(\text{CN})_2 + 3\text{H}_2\text{O}$ , is formed. When this is simply heated it decomposes, yielding potassium cyanide. It is not a difficult matter to make mercury cyanide,  $\text{Hg}(\text{CN})_2$ , from the potassium compound. By heating mercury cyanide it breaks up, yielding metallic mercury and cyanogen gas:



[What analogy is there between this reaction and that which takes place when mercury oxide is heated?]

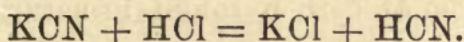
Cyanogen is a colorless gas. It receives its name from the fact that many of its compounds are blue (*κυανός*, blue). It is easily soluble in water and alcohol. It is extremely poisonous.

**Hydrocyanic Acid, Prussic Acid, HCN.**—This acid occurs in nature in combination with other substances,—in bitter almonds, the leaves of the cherry, laurel, etc. It is prepared by treating compounds of the metals and cyanogen with strong acids. Thus, by treating potassium cyanide with sulphuric acid this reaction takes place:



[Which reactions already considered does this suggest?]

Further, by treating potassium cyanide with hydrochloric acid, hydrocyanic acid is liberated:



[Which is the stronger acid, hydrochloric or hydrocyanic acid? Is sulphuric acid stronger than hydrochloric acid? Is it stronger than hydrocyanic acid?]

Hydrocyanic acid is a volatile liquid which boils at  $26.5^\circ$ , and solidifies at  $-15^\circ$ . It has a very characteristic odor resembling that of bitter almonds. It is extremely poisonous. It dissolves in water in all proportions, and it is such a solution which is known as prussic acid.

Both cyanogen and hydrocyanic acid are extremely unstable. In the presence of water, the nitrogen tends to combine with hydrogen to form ammonia, and the carbon with oxygen and hydrogen to form more stable compounds.

**Summary.**—Carbon is contained in all living things, and in their fossil remains. The number of compounds which

it forms is almost infinite. They are usually considered together under the head of Organic Chemistry.

Carbon is found in the atmosphere in the form of carbon dioxide, and in the form of carbonates, widely distributed in the earth.

Uncombined, it occurs in nature as diamond and graphite.

Amorphous carbon is a third variety of carbon. Charcoal in its various forms is amorphous carbon. It is made by charring organic substances which contain carbon, hydrogen, and oxygen. Coke, lamp-black, and bone-black are other forms of amorphous carbon. Bone-black has the power to extract coloring matters from solutions. Charcoal has the power to absorb gases, and is used for purifying air. It also absorbs disagreeable substances from water, and is used for the purpose of purifying water.

Coal is a form of carbon found in nature in many varieties. The soft coals contain more hydrogen than the hard coals, which contain a larger percentage of carbon.

At ordinary temperatures carbon is a very inactive element. At high temperatures it combines with oxygen with avidity. It is hence a good reducing agent, and is used extensively as such in the extraction of metals from their ores.

Carbon forms a large number of compounds with hydrogen. These are the *hydrocarbons*. Many of these are found in nature, as in petroleum, which is a complex mixture of hydrocarbons. Most of those which occur in petroleum belong to a series the members of which are closely related to one another. In composition they differ by  $\text{CH}_2$ , or a multiple of this. The series begins with marsh gas and is known as the marsh-gas series. A series

of this kind is known as an *homologous series*. There are several other homologous series of hydrocarbons. This kind of relation is characteristic of carbon compounds. Marsh gas is found in nature wherever organic matter undergoes decomposition without free access of air, as under water. It is found in coal-mines, and is a source of danger, as with air it forms an explosive mixture.

Carbon dioxide is formed in many natural processes, as in respiration, combustion, decay, and fermentation. It is prepared by treating a carbonate with an acid. The gas given off is not the acid, but a substance which bears to the acid the relation of an anhydride.

Carbon dioxide is the food of plants. Plants form the food of animals. Animals give back carbon dioxide to the air in the process of breathing. After death the carbon of animals and plants, if left exposed to the air, passes back to the form of carbon dioxide, and again starts on its round.

Carbon dioxide forms salts, with bases. These have the general formula  $M_2CO_3$ , in which M represents any metal, such as potassium, sodium, etc. These are very unstable, being decomposed by any acid. Carbonic acid is the weakest of all acids.

Calcium carbonate is insoluble in water, but it dissolves in water containing carbon dioxide. When heated the carbon dioxide is driven off and the calcium carbonate deposited. This phenomenon is the same as that which gives rise to the ordinary boiler incrustations.

Carbon monoxide is a poisonous gas, which is formed by incomplete oxidation of carbon or incomplete reduction of carbon dioxide. It is formed in ordinary coal fires by the passage of carbon dioxide over thoroughly heated coal.

It has strong affinity for oxygen, and is hence a good reducing agent.

A flame is a burning gas. A gas which burns in oxygen will form an atmosphere in which oxygen will burn. If a burning gas be cooled down even very slightly below its burning temperature, it is extinguished. The miner's safety-lamp consists of a flame surrounded by a piece of wire gauze. The gas cannot pass through this gauze without being cooled down below the burning temperature.

Flames are made up of different parts with different properties. The outer tip is the hottest part, and is called the oxidizing flame. The tip of the dark inner part, consisting of unburned gas, is the reducing flame.

A luminous flame can be made non-luminous by diluting the burning gas with neutral gases; by cooling the gases; by introducing oxygen into the gas so as to effect complete oxidation of the carbon.

In the presence of metals carbon and nitrogen combine to form cyanides. From these, cyanogen and hydrocyanic acid are obtained.

## CHAPTER XI.

### THEORY IN REGARD TO THE CAUSE OF THE LAWS OF DEFINITE AND MULTIPLE PROPORTIONS.— ATOMIC THEORY.—ATOMIC WEIGHTS.—MOLECULAR WEIGHTS.—MOLECULAR FORMULAS.

ONE of the most characteristic facts observed in chemical action is that it takes place between definite weights of substances. This subject has already been discussed, and it has been pointed out that, as the result of the examination of a large number of cases, it has been discovered that these two laws always hold good:

1. Chemical combination always takes place between definite masses of substances.
2. If two elements, A and B, combine in different proportions, the relative quantities of B which combine with any fixed quantity of A bear a simple ratio to one another.

These are the laws of definite and multiple proportions. They are simply condensed statements which sum up what has been found to be true in all cases examined. They are statements of facts discovered by actual experiment.

It is, however, one thing to know a general fact, and quite another to know the cause of the fact. We know that all bodies are attracted by the earth, and that they fall when thrown in the air. This is a very remarkable fact, and one of immense importance. We know that it is true, as we have evidence of its truth every day. But

yet we do not know why it is so. We say that the earth attracts other bodies by virtue of gravitation, but this does not tell us anything whatever about the cause of the phenomenon. We might verify the law of universal attraction over and over again without getting any nearer to the explanation. So, too, we might verify the important laws of definite and multiple proportions over and over again without being able to give an answer to the question, Why do substances combine according to these laws?

When we have established a law by means of experiments, and have accomplished all we can by means of experiments, the next thing in order is *to imagine a cause*. We try to imagine a condition of things which, if it existed, would lead to the results discovered. If we succeed in imagining such condition of things, we suggest an *hypothesis*. If, now, we test this hypothesis in every way that suggests itself, and find that all facts discovered are in accordance with it, we then call it a *theory*. An hypothesis is a guess in regard to the cause of certain phenomena. A theory is an hypothesis which has been thoroughly tested, and which is applicable to a large number of related phenomena.

Hypotheses and theories are of great value to science, if founded upon a thorough knowledge of the facts to which they relate. They become dangerous when used by those who are not familiar with the facts. Those whose minds have not been properly trained are apt to be given to unprofitable speculation. The student who has not received a thorough scientific training should remember that theories and hypotheses, to be of value, must be suggested, not by a superficial but by a thorough knowledge of facts.

With these words of warning and of explanation in re-

gard to the relation existing between the *fact*, the *law*, the *hypothesis*, and the *theory*, we may proceed to consider briefly a theory concerning the constitution of matter which grew out of the discovery of the laws of definite and multiple proportions.

**The Atomic Theory.**—If we consider any simple form of matter or element, such as iron, it is clear that there are two views which we may hold regarding the way the substance is made up. We know we can subdivide every piece of iron we can see, no matter how small it may be; and though after a time the particles might become so small that we could no longer subdivide them, still we can imagine that by more refined methods the process of subdivision might be continued indefinitely. If we believe that such infinite subdivision is possible, we hold the hypothesis that matter is infinitely divisible. We cannot prove this—we must speculate in regard to it. But we may also conceive that after the process of subdivision has been carried on for a time until very minute particles have been reached, a limit would be found beyond which the process of subdivision could not be carried. If we believe this, we hold the hypothesis that matter is not infinitely divisible, and this carries with it the belief that matter consists of *indivisible particles*. These particles may be called *atoms* (from the Greek *ἄτομος*, which signifies simply indivisible). Both of these hypotheses have been held for ages. But the discussion in regard to the relative merits of the two views was not much more profitable than it would be if carried on between two students who are in the early stages of their study of the facts.

When the laws of definite and multiple proportions were discovered by the English chemist Dalton, in the early

part of the present century, he saw that the conception that matter is made up of indivisible particles or atoms might have some connection with the laws. If each element is made up of atoms, the most probable view is that every atom of any particular element is exactly like every other atom of that element. Among the properties possessed by these atoms must be weight. It is probable that the atoms of different elements have different weights. Suppose now that, when chemical combination takes place between two elements, the real action takes place between these atoms, so that one atom of the one element combines with one of the other, and so on through the mass. If there were present in one mass exactly as many atoms as in the other, both substances would be used up—nothing would be left over. But if there were a larger number of atoms of one element than of the other, then, of the element of which the larger number of atoms is present, some would be left over after the action is complete. Suppose, further, that the weights of the atoms of two elements are to each other as 1 : 10. Then, if, when these two elements are brought together, they combine in the proportion of one atom of one to one atom of the other, the resulting compound would contain the elements in the proportion of one part by weight of one to ten parts by weight of the other. Or if, on analyzing a compound of two elements, we find that it contains one part by weight of one to ten parts by weight of the other, we might conclude that the weights of the atoms of the two elements bear to each other the ratio 1 : 10.

If matter consists of atoms, and chemical action takes place between these atoms, we can understand why chemical action takes place between definite weights of substances;

in other words, we see a probable reason for the law of definite proportions. As the atoms are supposed to be indivisible, if two elements combine in more than one proportion with each other, they must do so in the proportion of one atom of one to two atoms of the other, or one to three, or two to three, or in some other way which does not involve the breaking-up of the atoms. If, for example, two elements, the weights of whose atoms are as 1 to 10, combine in the proportion of one atom of one to one atom of the other, the resulting compound will contain the elements in the proportion of one part by weight of one to ten parts by weight of the other element. If the same elements combine in the proportion of one atom of the first to two atoms of the other, then the resulting compound will contain the elements in the proportion of one part by weight of one to twenty parts by weight of the other, and so on. It will thus be seen that if two elements combine in more than one proportion with each other, and the view that matter consists of atoms of definite weight, and that chemical action takes place between these atoms is correct, then it follows that the elements must combine in accordance with the law of multiple proportions.

**Atomic Weights.**—A thorough study of the facts has shown that the atomic theory, as suggested by Dalton, is the simplest conception which can be formed in regard to the constitution of matter which will satisfactorily account for the laws of definite and multiple proportions. The weights of the elements which have thus far been referred to as *combining weights* are, in accordance with the theory, the relative weights of the atoms, or the *atomic weights*. The symbols of the elements represent atoms of the elements. Thus H represents an atom of hydrogen, O an atom of

oxygen, Cl an atom of chlorine, etc. The combining weights, found by analyzing compounds in which these elements occur, are H = 1, O = 16, and Cl = 35.5. That is to say, by means of these figures we can always represent the relative quantities of the elements found in their compounds. Hydrochloric acid, for example, contains hydrogen and chlorine in the proportion of 1 part hydrogen to 35.5 parts chlorine. Hence it is believed that the weight of the atom of hydrogen is to that of chlorine as 1 to 35.5. As hydrogen enters into combination in smaller proportion than any other element, its combining weight or atomic weight is taken as the unit, and all others compared with it. If we say that the atomic weight of oxygen is 16, and that of chlorine is 35.5, we mean simply that the atom of oxygen is 16 times heavier and that of chlorine 35.5 times heavier than that of hydrogen. We might take any other standard, but that of the hydrogen atom is the simplest. At one time the atomic weight of oxygen was taken as 100, and then the atomic weights of the other elements were relatively larger.

[**PROBLEM.**—If we called the atomic weight of oxygen 100, what would those of hydrogen and chlorine be? The atomic weight of hydrogen being accepted as 1, those of oxygen and chlorine are 16 and 35.5 respectively.]

As the symbols of the elements represent atoms, so the symbols of compounds represent combinations of atoms. The formula of hydrochloric acid, HCl, represents, according to the theory, the smallest particle of this substance that can exist. It is made up of an atom of hydrogen and an atom of chlorine, which are chemically combined. The formulas  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$ , etc., represent the smallest particles of the substances that can exist. The smallest particle of nitric acid consists of 1 atom of hydrogen, 1 atom of

nitrogen, and 3 atoms of oxygen; the smallest particle of sulphuric acid that can exist consists of 2 atoms of hydrogen, 1 atom of sulphur, and 4 atoms of oxygen; the smallest particle of chloric acid consists of 1 atom of hydrogen, 1 atom of chlorine, and 3 atoms of oxygen. These smallest particles of compounds are called *molecules*. The formula  $\text{HNO}_3$  represents, then, a molecule of nitric acid,  $\text{H}_2\text{O}$  a molecule of water,  $\text{HCl}$  a molecule of hydrochloric acid. The molecules are made up of atoms. The weight of a molecule is equal to the sum of the weights of the atoms of which it is composed. The molecule of sulphuric acid is represented by  $\text{H}_2\text{SO}_4$ . The

2 atoms of hydrogen weigh.....	2 parts.
1 atom of sulphur weighs.....	32 "
4 atoms of oxygen weigh.....	64 "
	—
	98 "

The sum is 98. Therefore, the weight of the molecule of sulphuric acid is 98 times greater than the weight of the atom of hydrogen.

**How the Relative Weights of the Atoms are Determined.** —If we could isolate atoms and weigh them, there would be no serious difficulty in determining their relative weights. But as we cannot deal with atoms, we must deal with masses of atoms, and from a study of these masses draw conclusions regarding the weights of the atoms.

If it were the rule that two elements combine with each other in only one proportion, it might be safe to conclude that they combine in the proportion of one atom of one to one atom of the other. Then, by simply determining the relative weights of the elements contained in a mass of the compound, we would be in a position to draw a conclusion

regarding the relative weights of the atoms. But suppose two elements combine in more than one proportion. Suppose, for example, that nitrogen and oxygen combine, as they do, in these proportions: 14 of nitrogen to 8 of oxygen, 7 of nitrogen to 8 of oxygen, 7 of nitrogen to 16 of oxygen, and it is required from these figures to determine the relative weights of the atoms of nitrogen and oxygen. We may suppose that in the first compound the elements are combined atom to atom, then the relative weights of these atoms are 14 for nitrogen to 8 for oxygen. If, however, we had already concluded from a study of the compounds of hydrogen and oxygen that the atom of oxygen is 16 times heavier than that of hydrogen, we should have in the above compound of nitrogen and oxygen 28 parts of nitrogen combined with 16 parts of oxygen, and the atomic weight of nitrogen would appear to be 28. But we may equally well assume that in this compound 2 atoms of nitrogen are combined with 1 atom of oxygen. This idea would be represented by the formula  $N_2O$ , and, if we accept this conception, the atomic weight of nitrogen must be 14. This example will suffice to show that the determination of the relative weights of atoms by means of the analyses of compounds is a difficult matter, and that attempts to make the determinations in this way would necessarily lead us into difficulties which we could not surmount without the aid of some new conception which will aid us in judging of the number of atoms contained in the molecules of compounds.

**Avogadro's Hypothesis.**—Early in this century the Italian chemist Avogadro occupied himself with the study of the specific gravities of gaseous substances, and saw clearly that there is some connection between the figures representing

the relative weights of equal volumes of gases and those representing the combining weights. It has already been pointed out that the weights of equal volumes of hydrogen, chlorine, and oxygen bear to one another the same relation as their combining weights (atomic weights), viz., 1 : 35.5 : 16. The same relation is noticed in the case of other gases. This fact, taken together with others relating to the physical properties of gases, led Avogadro to the conception that *equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules*. This is known as Avogadro's hypothesis. It has been tested in a great many ways, but has always asserted itself as correct. The investigations of both chemists and physicists have only tended to confirm the correctness of the conception, and at the present day it forms one of the most important foundations of thought in regard to chemical phenomena. Let us see how it helps us, and what conclusions it leads us to.

We can determine the weights of equal volumes of gases without difficulty. According to the hypothesis of Avogadro, these weights bear to one another the same relation that the weights of the molecules of these substances do. Take, for example, some of the compounds thus far considered, which are gases at ordinary temperatures, or can be converted into gases by heat. These are water, hydrochloric acid, ammonia, nitrous oxide, nitric oxide, marsh gas, carbon dioxide, carbon monoxide, cyanogen, hydrocyanic acid. The specific gravities of these substances in the form of gas or vapor have been determined. They are water, 0.623; hydrochloric acid, 1.247; ammonia, 0.597; nitrous oxide, 1.520; nitric oxide, 1.039; marsh gas, 0.557; carbon dioxide, 1.529; carbon monoxide, 0.968; cyanogen,

1.8; hydrocyanic acid, 0.948. These figures, then, express the relative weights of equal volumes of the gases, and they also express the relation between the weights of the molecules of the substances. It is only necessary to adopt some standard to which we can refer the weights of other molecules. We may conveniently take hydrochloric acid. The smallest molecular weight which we can adopt for this compound without making the atomic weight of hydrogen less than unity is 36.5, for hydrochloric acid consists of 1 part by weight of hydrogen combined with 35.5 parts by weight of chlorine. Hence, if the sum of the weights of its atoms or its molecular weight were less than 36.5, the weight of the atom of hydrogen would be less than 1. If the molecular weight of hydrochloric acid is 36.5, it is an easy matter to calculate the molecular weights of the other substances mentioned, for, according to Avogadro's hypothesis, they bear to the molecular weight of hydrochloric acid the same relation that their specific gravities bear to the specific gravity of hydrochloric acid. The results of the calculation are given in the subjoined table:

COMPOUND.	Sp. Gr. of Gas or Vapor.	Calculated Molec. Weight.
Water.....	0.623	18.1
Hydrochloric acid.....	1.247	36.5
Ammonia.....	0.597	17.4
Nitrous oxide.....	1.52	44.5
Nitric oxide.....	1.039	30.4
Marsh gas.....	0.557	16.3
Carbon dioxide.....	1.529	44.8
Carbon monoxide.....	0.968	28.3
Cyanogen .....	1.8	52.6
Hydrocyanic acid.....	0.948	27.7

The figures thus deduced are relatively correct, provided always the hypothesis upon which the calculation is based is correct. Now, by analysis, we find that in 18 parts of

water there are 2 parts of hydrogen and 16 parts of oxygen; in hydrochloric acid there are 1 part of hydrogen and 35.5 parts of chlorine; in ammonia, 14 parts of nitrogen and 3 parts of hydrogen; in nitrous oxide, 28 parts of nitrogen and 16 parts of oxygen; in nitric oxide, 14 parts of nitrogen and 16 parts of oxygen; in marsh gas, 12 parts of carbon to 4 parts of hydrogen; in carbon dioxide, 12 parts of carbon and 32 parts of oxygen; in carbon monoxide, 12 parts of carbon and 16 parts of oxygen; in cyanogen, 24 parts of carbon and 28 parts of nitrogen; in hydrocyanic acid, 1 part of hydrogen, 12 parts of carbon, and 14 parts of nitrogen. Knowing the weights of the molecules into which an element enters, and the relative quantity of the element present in these molecules, we select the smallest quantity of the element that enters into the composition of molecules as the atomic weight. Thus, for example, if we were to examine all known oxygen compounds that can be studied in the form of gas or vapor, we should find that the smallest quantity of oxygen found in any molecule is represented by 16, using the standard already adopted. Thus, in water, to make up the molecular weight, 18, we have 16 parts of oxygen and 2 parts of hydrogen; in nitrous oxide, 28 parts of nitrogen and 16 parts of oxygen; in carbon dioxide, 12 parts of carbon and 32 parts of oxygen; in carbon monoxide, 12 parts of carbon and 16 parts of oxygen. We therefore select 16 as the atomic weight of oxygen.

The ratio of the specific gravity of a gas to its molecular weight is approximately 1 : 28.88, i.e.,

$$\frac{M}{d} = 28.88, \quad \text{or} \quad M = d \times 28.88, *$$

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\* The mere ability to state this rule is of no value to the student. What he should attempt to learn, and with an effort he can do so,

in which  $M$  represents the molecular weight of a gaseous compound, and  $d$  its specific gravity as compared with air as the standard. This gives us the molecular weight very nearly. The exact figure to be adopted is then determined by analysis.

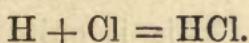
**Molecules of the Elements.**—The acceptance of Avogadro's hypothesis leads to a curious conclusion regarding the structure of elementary gases. If we determine the molecular weights of hydrogen, oxygen, chlorine, and nitrogen, we find that they are 2, 32, 71, and 28 respectively. In other words, they are twice as great as their atomic weights. According to this, these gases consist of molecules which are twice as heavy as their atoms, or, in other words, the molecules of these elementary gases consist of two atoms each. The same conclusion is reached by another line of reasoning. When one volume of hydrogen combines with one volume of chlorine, two volumes of hydrochloric acid are formed. Now, as equal volumes of all gases contain the same number of molecules, if we assume that in a certain volume of hydrogen there are 100 molecules, then in the same volume of chlorine and of hydrochloric acid there are also 100 molecules. But from 1 volume containing 100 molecules of hydrogen and 1 volume containing 100 molecules of chlorine we get 2 volumes containing 200 molecules of hydrochloric acid. In each molecule of hydrochloric-acid gas there must be at least one atom of hydrogen and one atom of chlorine, and in the 200 molecules of hydrochloric acid there must be 200 atoms of hydrogen and 200

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is the facts and the lines of thought which lead to the adoption of the rule. He should have a perfectly clear conception in regard to the meaning of the terms molecular weight and specific gravity, and the facts which led to the discovery of the relation existing between them.

atoms of chlorine. These 200 atoms of hydrogen, however, must have been contained in the 100 molecules of hydrogen with which we started, and similarly the 200 atoms of chlorine must have been contained in the 100 molecules of chlorine. Therefore, each molecule of hydrogen must consist of at least 2 atoms of hydrogen, and each molecule of chlorine must consist of at least 2 atoms of chlorine.

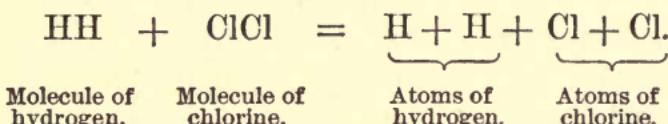
A similar study of other elementary gases leads to similar conclusions in regard to their molecules. The molecule of a few elementary gases has been shown to consist of 4 atoms, some of 3 atoms,\* and of a few others of a single atom; but usually the condition appears to be that found in hydrogen and chlorine. The view is thus forced upon us that the molecules of elementary gases consist of atoms of the same kind, just as the molecules of compound gases consist of atoms of different kinds. The molecule of hydrogen is a compound of two atoms of hydrogen, just as the molecule of hydrochloric acid is a compound of an atom of hydrogen and an atom of chlorine. According to this conception, when hydrogen gas and chlorine gas are brought together, the complete action is not represented by the equation



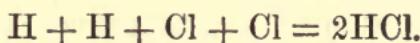
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\* In speaking of ozone, it was stated that when oxygen is changed to ozone there is a diminution of volume from three to two without change of weight. In other words, the specific gravity of oxygen is two thirds that of ozone. But the specific gravity of oxygen leads to the conclusion that its molecule contains two atoms. Similarly, the specific gravity of ozone leads to the conclusion that its molecule contains three atoms. We therefore conceive ozone to be made up of molecules each of which consists of three atoms of oxygen; and ordinary oxygen to be made up of molecules each of which consists of two atoms of oxygen. The molecular weight of ordinary oxygen is 32, and that of ozone is 48.

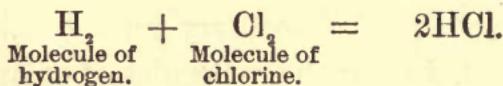
Before we can get atoms of hydrogen or chlorine, the molecules of hydrogen and chlorine must first be broken up. Hence, there are two acts involved in passing from hydrogen gas and chlorine gas to hydrochloric acid. These are:



Then, further, the atoms combine to form compound molecules :



Or we may write the equation thus :



Again, when an elementary gas such as hydrogen or oxygen is set free from a compound, we are led to believe from considerations like the above that at the instant it is liberated it exists in the atomic condition, but that if there is nothing else present with which the atoms combine, they combine with each other to form molecules. After it has been set free, therefore, it should be less active than at the instant it is set free. This is quite in accordance with some curious and well-known facts.

**Nascent State.**—It is found that at the instant elements are set free from their compounds they are capable of effecting changes which they cannot effect after they have once been set free. Thus, free oxygen gas passed into hydrochloric acid produces no change under ordinary conditions ; but oxygen liberated from a compound in contact with hydrochloric acid decomposes the latter and sets

chlorine free. Hydrogen gas passed into nitric acid causes no change ; but hydrogen liberated in direct contact with nitric acid reduces the acid and forms the lower oxides of nitrogen. Many other examples of this kind of action might be cited. The simplest explanation of the phenomenon is that offered above. An element at the instant of its liberation is said to be in the *nascent state*.

According to what has been said, all substances, elementary as well as combined, appear to be made up of molecules. The molecules are believed to have the properties of the substance as we know it in the free state. The molecule is the smallest particle of a substance that can exist in the free state. The molecules are said to be held together by cohesion, and, theoretically, a substance could be separated into its molecules by purely mechanical processes. As long as action upon a substance does not pass beyond the molecules, does not involve decomposition of the molecules, the action is in the realm of physics. The molecules are made up of atoms, which are held together by chemical affinity. The atom enters into chemical action and is the smallest particle of a substance that can do so. Chemistry is the science which has to deal with changes within the molecules. It must be remembered that these statements are not statements of facts known to us. The laws of definite and multiple proportions are statements of facts; but when we come to speak of atoms and molecules we are dealing with conceptions which, however probable they may appear, can nevertheless not be proved to be true. We make use of these conceptions because they simplify our dealings with the facts of chemistry, and suggest lines of inquiry which lead to discoveries of value.

**How a Formula is Determined.**—Chemical formulas

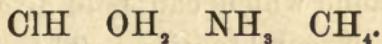
were first introduced for the purpose of expressing the composition of substances. They might be used for this purpose at present without having any connection whatever with the conception of atoms and molecules, but the difficulty would then be to decide upon the combining weights of the elements. It would be possible for authoritative bodies to unite in issuing an edict that the combining weights of the elements shall be certain figures which are in harmony with facts known. But this would hardly be a scientific mode of procedure; and there might exist differences of opinion in regard to the advisability of accepting the figures. When, however, we once accept the atomic theory and the hypothesis of Avogadro, we have a definite basis to work on, and there is little opportunity for disagreement in regard to the figures to be adopted.

The necessary steps in the determination of the formula of a compound may be illustrated by the case of water. The compound is first analyzed and found to contain hydrogen and oxygen in the proportion of 1 part hydrogen to 8 parts oxygen. This is a fact. But we wish to express by our formula not only the composition of the substance, but the composition of a molecule of the substance. We therefore determine the molecular weight by the method described above by comparing the specific gravity of its vapor with that of hydrochloric acid or hydrogen. We find that the molecular weight is 18. In other words, the molecule of water, or the smallest particle of water, is 18 times heavier than an atom of hydrogen. According to the analysis, the 18 parts are made up of 2 parts of hydrogen and 16 parts of oxygen. By an examination of a large number of gaseous compounds containing oxygen we conclude that 16 is the atomic weight of oxygen, as this is the smallest

quantity found in any of the compounds. Therefore, the molecule of water consists of 2 atoms of hydrogen weighing 2 parts and 1 atom of oxygen weighing 16 parts. The formula representing the facts and conceptions in regard to the composition of water is  $H_2O$ .

Every formula is intended to express the composition and relative weight of a molecule of the compound represented. But only in the case of compounds which are gases or which can be converted into vapors have we a definite basis for assuming that the formulas do represent the relative weights of the molecules.

**Valence.**—The formulas of the compounds thus far considered have all been determined by exactly the same methods. On comparing the formulas of the hydrogen compounds of chlorine, oxygen, nitrogen, and carbon, we cannot fail to be struck by certain curious differences between them. The formulas are



Speaking in terms of the theory, the molecule of hydrochloric acid consists of 1 atom of chlorine combined with 1 atom of hydrogen; the molecule of water consists of 1 atom of oxygen combined with 2 atoms of hydrogen; the molecule of ammonia consists of 1 atom of nitrogen combined with 3 atoms of hydrogen; the molecule of marsh gas consists of 1 atom of carbon combined with 4 atoms of hydrogen. We see, thus, that the atoms of chlorine, oxygen, nitrogen, and carbon differ from one another in their power of holding hydrogen in combination. The oxygen atom has twice the power of the chlorine atom, the nitrogen atom has three times this power, and the carbon atom has four times this power. On examining the

compounds of other elements, we find that other atoms differ from one another in the same way.

The smallest power, as far as the number of other atoms which it can hold in combination is concerned, is that of the chlorine atom. And as one chlorine atom can hold but one atom of hydrogen in combination, so one atom of hydrogen can hold but one atom of chlorine in combination. Either the hydrogen atom or the chlorine atom may be taken as an example of the simplest kind of atom. Any element like hydrogen and chlorine is called a *univalent element*; an element like oxygen whose atom can hold two unit atoms in combination is called a *bivalent element*; an element like nitrogen whose atom can hold three unit atoms in combination is called a *trivalent element*; an element like carbon whose atom can hold four unit atoms in combination is called a *quadrivalent element*. Most elements belong to one or the other of these four classes, though there are some which can hold five, six, and even seven unit atoms in combination. These are, however, rare, and for our present purpose they will require but slight notice.

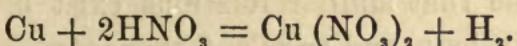
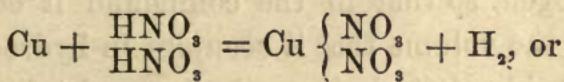
*Valence* is that property of an element by virtue of which its atom can hold a definite number of other atoms in combination.

[Calcium forms with chlorine the compound  $\text{CaCl}_2$ . What is the valence of calcium? Potassium and sodium form chlorides of the formulas  $\text{KCl}$  and  $\text{NaCl}$  respectively. What is the valence of these elements? Sulphur forms with hydrogen a compound of the formula  $\text{SH}_2$ . What is the valence of sulphur?]

**Replacing Power of Elements.**—In the formation of salts, we have seen that the hydrogen of acids is replaced by

metals. In such cases one atom of a univalent metal takes the place of one atom of hydrogen, one atom of a bivalent metal takes the place of two atoms of hydrogen, etc. Thus, potassium and sodium are univalent. An atom of either takes the place of one atom of hydrogen in forming salts. In the formation of potassium nitrate from nitric acid,  $\text{HNO}_3$ , one atom of potassium replaces the one atom of hydrogen in the molecule of nitric acid forming the salt  $\text{KNO}_3$ . So, also, in sodium nitrate,  $\text{NaNO}_3$ , one atom of the univalent element sodium replaces one atom of hydrogen. In the molecule of sulphuric acid,  $\text{H}_2\text{SO}_4$ , there are two atoms of hydrogen. To replace these, two atoms of a univalent element are required. Thus, potassium sulphate is  $\text{K}_2\text{SO}_4$ , and sodium sulphate is  $\text{Na}_2\text{SO}_4$ . Illustrations of salts containing bivalent metals are the following: Zinc sulphate,  $\text{ZnSO}_4$ , in which one atom of the bivalent element zinc replaces the two atoms of hydrogen in sulphuric acid; barium sulphate,  $\text{BaSO}_4$ , in which one atom of bivalent barium replaces the two atoms of hydrogen of sulphuric acid.

When a bivalent metal forms a salt with an acid like nitric acid, which contains but one atom of hydrogen in the molecule, it is believed that one atom of the metal acts upon two molecules of the acid, thus:



The formula of zinc nitrate is similar, viz. :  $\text{Zn}(\text{NO}_3)_2$ . In the case of trivalent elements the matter is a little more complicated, but still simple enough if it be borne in mind that a univalent atom replaces one atom of

hydrogen ; a bivalent atom replaces two atoms of hydrogen ; a trivalent atom replaces three atoms of hydrogen, etc., etc. We have already had some examples illustrating these principles. We shall meet with others particularly in connection with the subject of salts.

We have no idea what the cause of the property called valence is. The property is undoubtedly due to some deep-seated condition of the atoms. The univalent, bivalent, trivalent, and quadrivalent elements probably differ from one another in some fundamental way. This is indicated by a consideration of the volumes of hydrogen, chlorine, oxygen, and nitrogen which combine with one another. As we have seen, 1 volume of hydrogen combines with 1 volume of chlorine, forming 2 volumes of hydrochloric acid. This is the simplest relation conceivable. Further, 1 volume of oxygen combines with 2 volumes of hydrogen, forming 2 volumes of water vapor. In this case we get 2 volumes of the product from 3 volumes of the combining gases. Apparently the oxygen so influences the hydrogen as to cause it to occupy only half the volume which it does in hydrochloric acid. In the combination of nitrogen and hydrogen to form ammonia 3 volumes of hydrogen combine with 1 volume of nitrogen to form 2 volumes of ammonia. The nitrogen apparently influences the hydrogen, so that in the compound it occupies only one third the volume that it occupies in hydrochloric acid. It is probable that similar relations exist between other univalent, bivalent, and trivalent elements.

The subject of valence is a difficult one to deal with, for the reason that the valence of an element is not fixed, but varies according to circumstances. It may vary (1) according to the temperature. In general, the higher the

temperature the less the valence. Thus, phosphorus, which is quinvalent towards chlorine at ordinary temperatures, as is shown by the formation of the compound  $\text{PCl}_5$ , is trivalent towards the same element at higher temperature, as is shown by the fact that when heated the compound  $\text{PCl}_5$  gives off chlorine and becomes  $\text{PCl}_3$ .

The valence of the element may vary (2) according to the chemical character of the element with which it combines. Thus, phosphorus, which is quinvalent towards chlorine at ordinary temperatures, is trivalent towards hydrogen, as is shown by the compound  $\text{PH}_3$ .

Generally speaking, however, each element shows a tendency to act with a particular valence ; or if it varies at all, the variation is between narrow limits. Nitrogen appears as trivalent and quinvalent ; carbon as bivalent and quadrivalent, etc.

**Summary.**—When natural laws are discovered we try to find out the causes. In suggesting a possible cause we form an hypothesis. When the hypothesis has been well tested and applies to a large number of related facts, it is called a theory. The atomic theory was proposed to account for the laws of definite and multiple proportions. According to the atomic theory as accepted by chemists, all substances consist of atoms or indivisible particles with definite weights. When chemical action takes place it does so between these particles, and it consists either in a separation or a union of these particles. The relative weights of atoms are called the *atomic weights*. The smallest particles of compounds are called molecules. It is impossible by means of analysis alone to reach definite conclusions in regard to the relative weights of atoms.

Avogadro's hypothesis that equal volumes of all gases

under the same conditions of temperature and pressure contain the same number of molecules was suggested by a study of the physical properties of gases and a comparison of the weights of equal volumes of gases, or their specific gravities, with the combining weights as found by analysis. The molecular weights of substances bear to one another the same relations that the specific gravities of their gases or vapors do. Owing to a peculiarity of gases and vapors which we cannot discuss here, their specific gravities are not exactly proportional to their molecular weights. They are very nearly so. From the specific gravity we calculate the molecular weight, and then by analyzing the compounds we determine exactly what the molecular weight is.

After analyzing the compounds of an element and determining their molecular weights, we select the smallest quantity of the element that occurs in any of the compounds as the atom, and the weight of this quantity as compared with the weight of the smallest quantity of hydrogen found in any of its compounds taken as unity is the atomic weight of the element.

Elementary gases and vapors are made up of molecules, which in turn consist of atoms of the same kind. Elements are more active in the nascent state than in the free state, probably because the instant they are set free the atoms are uncombined, while after they have been set free these atoms are combined in the form of molecules.

Formulas of compounds are intended to represent the composition of molecules and their relative weights. They rest upon analyses and determinations of the specific gravity of the substances in the form of gas or vapor.

The valence of an element is the property by virtue of which its atom has the power to hold in combination a cer-

tain number of other atoms. Elements are called univalent, bivalent, trivalent, quadrivalent, etc., according as they exhibit the simplest valence like that of hydrogen and chlorine, or double, treble, or quadruple this valence.

The replacing power of the elements is determined by the valence. An atom of a univalent element can replace one atom of hydrogen; an atom of a bivalent element can replace two atoms of hydrogen.

## CHAPTER XII.

### CLASSIFICATION OF THE ELEMENTS.

ANY attempt to classify objects without a thorough knowledge of their properties must necessarily be imperfect. We may classify men according to various properties,—for example, as tall and short, as stupid and intelligent, as strong and weak, as white and colored, etc.; but any such classification is obviously imperfect, for the reason that it takes into account only a few properties of men. So, also, in attempting to classify the elements it is difficult to reach a satisfactory result, for the reason that if we make one set of properties the basis of classification, it is questionable whether there may not be more fundamental properties which should furnish the basis. As our knowledge in regard to the fundamental properties of the elements increases, the problem of classification will become simpler.

The chemical properties which force themselves upon our attention most prominently in whatever field of chemistry we may be working are those which are known as *acid properties* and *basic properties*. As has already been pointed out, these two kinds of properties are complementary. Acid properties are the opposite of basic properties, and they have the remarkable power of being able to destroy each other when the substances possessing them are brought together. Whatever developments there may be in

the study of chemistry in the future, it is certain that the distinction between these two kinds of properties will always be recognized as important. In general, both acids and bases contain oxygen and hydrogen. *There are some elements whose compounds with hydrogen and oxygen have basic properties, and others whose compounds with hydrogen and oxygen have acid properties.* This important fact may be used as a basis for a partial classification of the elements. According to this, we have (1) *acid-forming elements* and (2) *base-forming elements*. As examples of the first class, the elements chlorine, nitrogen, and carbon, already considered, may be mentioned. Examples of the second class are sodium, calcium, magnesium, copper, iron, zinc, etc. The last-mentioned elements are generally called *metals*, and those mentioned as examples of acid-forming elements are generally called *non-metals*. The line between acid-forming and base-forming elements cannot be drawn sharply, for there are some elements which form both acids and bases, according to the relative quantity of oxygen with which they combine. Thus, antimony forms acids with well-marked properties, and also other compounds which neutralize acids, and are therefore bases. The same is true of chromium, manganese, and some other elements. On the other hand, there are several elements which form only acids, and several which form only bases; and, further, those which form both acids and bases generally show a tendency in one direction. In dealing with the elements, then, these differences in properties will be taken into account.

Another important fact which is soon recognized in studying the elements is that they fall into families according to their general chemical properties, the members of

the same family showing striking resemblances among one another. Thus, we have the chlorine family, which includes, besides chlorine itself, bromine, iodine, and fluorine. We shall soon see that these three elements resemble chlorine very closely indeed, so that what we have already learned in regard to chlorine will be of great assistance to us in studying the other members of the family. Further, we have the sulphur family, consisting of the closely related elements sulphur, selenium, and tellurium; the potassium family, consisting of lithium, sodium, potassium, rubidium, and caesium; the calcium family, consisting of calcium, barium, strontium; and others. In all these cases the resemblance between the members of the same family is striking. While it is an easy matter to recognize the existence of these families, the recognition of any connection between the different families is more difficult; and, hence, attempts to bring all the elements into one general scheme of classification have been unsatisfactory. It would be premature to discuss the subject at this stage, as the discussion would necessitate reference to many matters which are not familiar to the student. The plan which will be followed is briefly this: The elements thus far considered, with the exception of hydrogen, serve as types of certain classes, or as representatives of families. Hydrogen has no analogue among the other elements. It is not a member of any family. Oxygen, too, has certain peculiarities which distinguish it from most other elements. It nevertheless shows some resemblance to sulphur in the character of its compounds, and the two are usually regarded as belonging to the same family. Chlorine, as already stated, belongs to a family of which bromine, iodine, and fluorine are the other members. Nitrogen be-

longs to a family of which phosphorus, arsenic, and antimony are the other best-known members. Carbon also belongs to a family, silicon being the other well-known member. We therefore have the following families first to deal with :

CHLORINE FAMILY.	SULPHUR FAMILY.	NITROGEN FAMILY.	CARBON FAMILY
Chlorine,	Sulphur,	Nitrogen,	Carbon,
Bromine,	Selenium,	Phosphorus,	Silicon.
Iodine,	Tellurium.	Arsenic,	
Fluorine.		Antimony.	

The principal members of these families are acid-forming elements, generally called non-metals, or metalloids. In the nitrogen family, however, one of the members is both acid-forming and base-forming. There is a gradation in the properties as we pass from nitrogen to antimony.

As the object of this book is, not to present a systematic treatise on the facts of chemistry, to serve as a book of reference, but rather to present concisely such facts as serve to illustrate the general character of chemical action and the general principles of the science of chemistry, it will not be necessary to go into details in dealing with these families. One member of each family having been treated comparatively fully, the other members may be treated briefly. It will thus be possible to get a clearer idea of the principles of the science than by attempting to study a large number of facts the connection between which can be but dimly discerned, if discerned at all.

After the acid-forming elements have been considered, the base-forming elements will be taken up in a similar way; but, as will be seen, the chemistry of the acid-forming elements exhibits more variety, and is hence better adapted to the illustration of the general principles of the science than that of the base-forming elements, so that the latter need not be treated as fully.

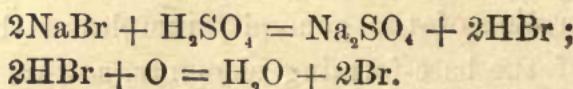
## CHAPTER XIII.

### THE CHLORINE FAMILY: CHLORINE, BROMINE, IODINE, FLUORINE.

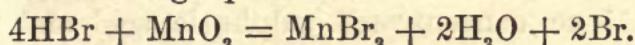
THE three members of this family which show the most marked resemblance are chlorine, bromine, and iodine. Fluorine is not known in the free state, but only in compounds. These, however, resemble the compounds of chlorine in some respects, and hence the element is generally included in this family.

**Bromine, Br (At. Wt. 80).**—This element occurs in nature in company with chlorine. Chlorine, as has been stated, occurs mostly in combination with sodium, as sodium chloride, or common salt. In several of the great salt-beds there is some bromine in the form of sodium bromide, NaBr, and in some places it occurs as potassium bromide, KBr.

The process of preparation of bromine is exactly the same as that made use of for extracting chlorine. It will be remembered that in order to get chlorine out of sodium chloride the salt is first converted into hydrochloric acid, and this is then oxidized. So, too, in order to get bromine out of sodium bromide, it must first be converted into hydrobromic acid, and this then oxidized. The reactions involved are usually:



As in the case of chlorine, the substance commonly used is manganese dioxide, when the reaction takes place according to the following equation :



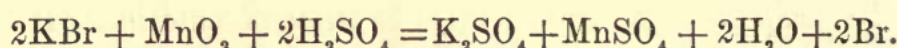
[Refer back to the explanation of this reaction given under the head of chlorine. What other methods might be used in the preparation of bromine ?]

Bromine is a heavy dark red liquid at ordinary temperatures. It is easily converted into vapor which is brownish red. At  $-24^{\circ}$  it is solid. It has an extremely disagreeable smell, to which fact it owes its name (from  $\beta\rho\omega\mu\sigma$ , a stench).

Its properties are, in general, like those of chlorine. It acts violently upon organic substances. It attacks the skin and the membranes lining the passages of the throat and lungs in much the same way as chlorine. Wounds caused by the liquid coming in contact with the skin are painful and serious. It must be handled with great care. With water at low temperatures it forms a hydrate corresponding to chlorine hydrate, of the formula  $\text{Br}_2 \cdot 10\text{H}_2\text{O}$ , which decomposes when left in contact with the air at ordinary temperatures. It dissolves slightly in water, forming a colored solution called bromine water.

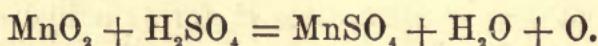
Its chemical conduct is also like that of chlorine. It combines with many elements directly and with great avidity. Its combination with arsenic and some other elements is accompanied by an evolution of light and heat, as in the case of chlorine. Its compounds with other elements are called *bromides*. While acting in general in the same way as chlorine, it is a somewhat weaker element, so that chlorine drives it out of its compounds and sets it free.

**EXPERIMENT 102.**—Mix together 3.5 grams potassium bromide and 7 grams manganese dioxide. Put the mixture into a 500 cc. flask ; connect with a condenser (see Fig. 22). Mix 15 cc. concentrated sulphuric acid and 90 cc. water. After cooling pour the liquid on the mixture in the flask. Gently heat, when bromine will be given off in the form of vapor. A part of this will condense and collect in the receiver. Perform this experiment under a hood with a good draught. In treating the manganese dioxide and potassium bromide together with sulphuric acid, the action takes place as represented in the following equation :



Hence there are left behind in the flask both potassium sulphate,  $\text{K}_2\text{SO}_4$ , and manganese sulphate,  $\text{MnSO}_4$ .

[When sulphuric acid acts upon manganese dioxide the action takes place thus :

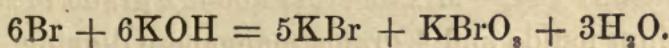


If this action took place in the presence of hydrobromic acid, what effect would the liberated oxygen have ? Suppose the oxygen were allowed to escape from the flask containing the manganese dioxide and sulphuric acid, and then passed into hydrobromic acid, would the same result be reached as when the hydrobromic acid is in the flask in which the oxygen is liberated ? What is the commonly accepted explanation ? If the formula of manganese sulphate is  $\text{MnSO}_4$ , what is the valence of manganese ? What would you expect the formula of manganese chloride to be ? Of manganese oxide ? Is the valence of manganese greater toward oxygen or toward chlorine ?]

**Hydrobromic Acid, HBr.**—The only compound which bromine forms with hydrogen alone is hydrobromic acid. This is in all respects very much like hydrochloric acid. It is made in the same way. It is a colorless gas, which forms fumes in the air in consequence of its attraction for moisture. Its solution in water acts very much like ordinary hydrochloric acid. The elements are not held together as firmly in hydrobromic as in hydrochloric acid. This is shown by its decomposition under circumstances in which hydrochloric acid is stable. Thus, for example, it is decomposed by sulphuric acid, while hydrochloric acid is not. The hydrogen is separated from the bromine and acts upon the sulphuric acid, while the bromine is given off as such. Hence, when potassium bromide is treated with sulphuric acid, hydrobromic acid is given off, together with bromine and a compound of sulphur and oxygen which is formed by the action of hydrogen on the sulphuric acid.

**EXPERIMENT 103.**—In a small porcelain evaporating-dish put a few crystals of potassium bromide. Pour on them a few drops of concentrated sulphuric acid. The white fumes of hydrobromic acid and the reddish-brown vapor of bromine are noticed. Treat a few crystals of potassium or sodium chloride in the same way. What difference is there between the two cases?

**Compounds with Hydrogen and Oxygen.**—With hydrogen and oxygen bromine forms compounds which resemble very closely those which chlorine forms with the same elements. The principal ones are *bromic* and *hypobromous acids*. The potassium salt of bromic acid,  $\text{HBrO}_3$ , is formed by treating a strong solution of caustic potash with bromine:



The potassium salt of hypobromous acid,  $\text{HBrO}$ , is formed by treating a dilute solution of caustic potash with bromine:



**Iodine, I (At. Wt. 127).**—This element occurs in nature in combination with sodium, in company with chlorine and bromine, but in smaller quantity than either. It is also found in larger quantities in all sea plants. It is obtained largely from the latter source. On the coasts of Scotland and France the sea-weed which is thrown up by storms is gathered, dried, and burned. The organic portions are thus destroyed [What is the meaning of the word destroyed used in this sense?] and the mineral or earthy portions are left behind as ashes. This incombustible residue is called *kelp*. It contains sodium iodide. Sea-weed is also cultivated for the sake of the sodium iodide contained in it. Chili salt-petre, or the natural sodium nitrate found in Chili, contains some sodium iodide, and of late this has furnished a considerable quantity of the iodine of commerce.

Iodine is obtained from sodium iodide just as chlorine and bromine are obtained from their compounds with sodium and potassium. [Give the equations representing the steps which must be taken in order to separate iodine from sodium iodide.]

At ordinary temperatures iodine is a grayish-black crystallized solid. It is volatile at ordinary temperatures. It melts at a temperature a few degrees above that of boiling water, and boils at a somewhat higher temperature, when it is converted into a violet vapor.

**EXPERIMENT 104.**—Mix together about 2 grams of sodium or potassium iodide and 4 grams manganese dioxide. Treat

with a little sulphuric acid in a one to two litre flask. Heat gently on a sand-bath. Gradually the vessel will be filled with the beautiful colored vapor of iodine. In the upper parts of the flask some of the iodine will be deposited in the form of crystals of a grayish-black color.

The action of iodine is, in general, the same as that of chlorine and bromine, only its affinities are weaker. Hydrobromic acid, as we have seen, is a weaker compound than hydrochloric acid. Hydriodic acid is still weaker. Chlorine acting upon hydromic acid sets bromine free. Chlorine and bromine set iodine free from hydriodic acid.

Iodine dissolves slightly in water, easily in alcohol, and easily in a water solution of potassium iodide.

**EXPERIMENT 105.**—Make solutions of iodine in water, in alcohol, and in a water solution of potassium iodide. Use small quantities in test-tubes.

When a solution containing *free iodine* is treated with a little starch paste, the solution turns blue, in consequence of the formation of a complicated compound of starch and iodine. Bromine and chlorine do not form blue compounds. Advantage is taken of this fact to distinguish between iodine and other members of the same family.

**EXPERIMENT 106.**—Make some starch paste by covering a few grains of starch in a porcelain evaporating-dish with cold water, grinding this to a paste, and pouring 200–300 cc. boiling hot water on it. After cooling add a little of this paste to a dilute water solution of iodine. The solution will turn blue if the conditions are right. Now add a little of the paste to a diluted water solution of potassium iodide. There is no change of color, because the iodine is in combination with the potassium. Add a drop or two of a solution of chlorine in water, when the blue color will

appear. The explanation of this phenomenon is that the chlorine sets the iodine free, and the free iodine then acts upon the starch, producing the blue compound. [How can you show that the chlorine itself will not form a blue compound with starch?]

**Hydriodic acid, HI,** is analogous to hydrochloric and hydrobromic acids. It is set free from its compounds by treating them with sulphuric acid, but it is even more unstable than hydrobromic acid, and hence breaks up into hydrogen and iodine. The iodine is liberated, while the hydrogen acts on the sulphuric acid, as it does in the case of hydrobromic acid.

**EXPERIMENT 107.**—Treat a few crystals of potassium iodide with sulphuric acid. [What do you notice?] Compare the result with that obtained in the case of potassium bromide and sodium chloride.

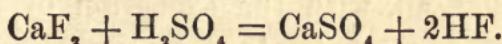
The principal compound of iodine with hydrogen and oxygen is iodic acid,  $\text{HIO}_3$ , which is the analogue of chloric and bromic acids. It is known principally in the form of its potassium salt, potassium iodate,  $\text{KIO}_3$ . When heated, this salt, like the chlorate and the bromate, gives up all its oxygen, potassium iodide,  $\text{KI}$ , being left behind.

**Fluorine** occurs in nature in large quantity, and widely distributed, but always in combination with other elements. It is found chiefly in combination with calcium, as *fluor-spar*, or *calcium fluoride*,  $\text{CaF}_2$ , and in combination with sodium and aluminium, as *cryolite*, a mineral which occurs abundantly in Greenland, and has the composition  $3\text{NaF} \cdot \text{AlF}_3$ , being a complex compound of sodium fluoride and aluminium fluoride.

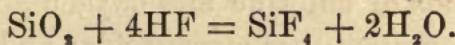
All attempts to obtain fluorine in the free state have

failed. This appears to be due to the extraordinary power which fluorine has of combining with other substances. This power causes it to combine with the materials of which the vessels in which it is liberated are made.

**Hydrofluoric acid, HF,** is made from fluor-spar by treating it with sulphuric acid. The action is of the same character as that which takes place when hydrochloric acid is liberated from sodium chloride:



It is a colorless gas, with strong acid properties. It greatly irritates the membranes lining the respiratory organs, and hence care should be taken not to inhale it. It acts upon glass, dissolving it, and must therefore be kept in vessels of rubber, lead, or platinum, upon which it does not act. Its action on glass consists in the transformation of silicon dioxide, or silica,  $\text{SiO}_2$ , which is contained in all kinds of glass, into *silicon tetrafluoride*,  $\text{SiF}_4$ , which is a gas. The action is represented thus:



**EXPERIMENT 108.**—In a lead or platinum vessel put a few grams (5–6) of powdered fluor-spar and pour on it enough concentrated sulphuric acid to make a thick paste. Cover the surface of a piece of glass with a thin layer of wax or paraffin, and through this scratch some letters or figures, so as to leave the glass exposed where the scratches are made. Put the glass over the vessel containing the fluor-spar, and let it stand for some hours. Take off the glass, scrape off the coating, and the figures which were marked through the wax or paraffin will be found *etched* on the glass.

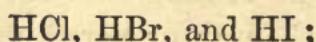
The acid is used for etching glass, particularly for marking scales on thermometers, barometers, and other graduated glass instruments. A solution of the gas in water is manufactured for this purpose and kept in rubber bottles.

Fluorine does not combine with oxygen. It is the only element of which this statement can be made.

**Comparison of the Members of the Chlorine Family.**—In considering, first, the physical properties of these elements, we notice that all, with the exception of fluorine, form colored gases or vapors. At ordinary temperatures chlorine is a gas, bromine a liquid, and iodine a solid. In regard to their chemical conduct, it may be said that, in general, fluorine exhibits the strongest affinity for elements with which it combines at all; chlorine comes next in order, then bromine, and lastly iodine. This is seen particularly in the relative stability of their compounds with hydrogen. Their compounds with metals also show the same relation. On the other hand, with oxygen the order is reversed. Fluorine does not unite with oxygen at all. The compounds of chlorine and oxygen are very unstable; those with bromine rather more stable; and one compound of iodine and oxygen is comparatively stable.

The elements of this family combine with hydrogen and with other elements in the simplest way. *They are all univalent.*

The compounds formed by the three elements chlorine, bromine, and iodine with hydrogen and oxygen have analogous composition, and are formed by analogous reactions. Thus, we have the hydrogen compounds:



and the compounds with hydrogen and oxygen:

HClO	HBrO	—
HClO <sub>2</sub>	—	—
HClO <sub>3</sub>	HBrO <sub>3</sub>	HIO <sub>3</sub>
HClO <sub>4</sub>	HBrO <sub>4</sub>	HIO <sub>4</sub>

The properties of any compound of one element are similar to those of the compounds of analogous composition of the other elements of the family.

All these facts seem to indicate that these elements are not distinct forms of matter entirely independent of one another, but rather that they contain some common constituent. This idea is apparently confirmed by a consideration of their combining or atomic weights, which are as follows:

Chlorine, 35.5;  
Bromine, 80;  
Iodine, 127.

On comparing these it will be seen that the atomic weight of bromine, 80, is nearly the mean of the atomic weights of chlorine and iodine, or at least near enough to arrest attention. We have  $35.5 + 127 = 162.5$ , and  $\frac{162.5}{2} = 81.25$ . *The properties of these elements vary with the variations in their atomic weights, or with the weights of their atoms.* The gradation in properties takes place in the order chlorine, bromine, iodine, and this is also the order in which the atomic weights increase. This may be a mere accident, but we shall find that in the other families we meet with similar indications of a close connection between the weights of the atoms of the elements and their physical and chemical properties. And so closely has this connec-

tion been traced out that it now appears possible to foretell the properties of an element if we know its atomic weight. Why there should be this remarkable connection we do not know. Doubtless, continued investigation of chemical phenomena will eventually lead to the discovery of some reason for it. At present the facts have not been studied sufficiently deeply to enable us to form any probable conception in regard to the cause. It is not impossible that what we call elements may be compounds of a few still simpler substances; but however attractive such speculation may be, it is not profitable unless it leads to further work for the purpose of proving its soundness or of refuting it. The discovery of a direct relation in composition between the members of the same family of elements would furnish a basis for profitable speculation. Such a discovery would rank in importance with the discovery that heat and motion are convertible one into the other.

## CHAPTER XIV.

### THE SULPHUR FAMILY: SULPHUR, SELENIUM, TELLURIUM.

**Sulphur, S. (At. Wt. 32).**—The principal member of this family is sulphur. In nature it is frequently found accompanied by small quantities of selenium, and sometimes by tellurium. It has been known in the elementary form from the earliest times, for the reason that it occurs abundantly in this form in nature. It is found particularly in the neighborhood of volcanoes, as in Sicily, which is the chief source of the sulphur of commerce. It occurs, further, in combination with many metals as sulphides,—as in iron pyrites,  $\text{FeS}_2$ ; copper pyrites,  $\text{FeCuS}_2$ ; galenite,  $\text{PbS}$ , etc.; in combination with metals and oxygen as sulphates,—for example, as calcium sulphate, or gypsum,  $\text{CaSO}_4 + 2\text{H}_2\text{O}$ ; barium sulphate, or heavy spar,  $\text{BaSO}_4$ ; lead sulphate,  $\text{PbSO}_4$ ; in a few vegetable and animal products in combination with carbon, hydrogen and, generally, with nitrogen.

**Extraction of Sulphur from its Ores.**—When taken from the mines, sulphur is mixed with many earthy substances from which it must be separated. This separation is accomplished by piling the ore in such a way as to leave passages for air. The piles are covered with material to prevent free access of air, and the mass is then lighted below. A part of the sulphur burns, and the heat thus furnished melts the rest of the sulphur. The molten sulphur runs

down to the bottom of the pile, and is drawn off from time to time. If the pile were not protected from free access of air, the sulphur would burn up, yielding a gas, sulphur dioxide,  $\text{SO}_2$ .

[What analogy is there between this process and that made use of in making charcoal? What are the essential differences between the two processes?]

The crude brimstone thus obtained is afterwards refined by distillation, and it is this distilled sulphur which we meet with in the market under the names "roll brimstone" and "flowers of sulphur." The distillation is carried on in earthenware retorts connected with large chambers of brick-work. When the vapor of sulphur first comes into the condensing-chamber it is suddenly cooled, and hence deposited in the form of a fine powder. This is what is called "flowers of sulphur." After the distillation has continued for some time, the vapor condenses in the form of a liquid, which collects at the bottom of the chamber. This is drawn off into wooden moulds and takes the form of "roll brimstone" or "stick sulphur."

**Properties.**—Sulphur is a yellow, brittle substance which at  $-50^\circ$  is almost colorless. It melts at  $111^\circ$ , forming a thin, straw-colored liquid. When heated to a higher temperature it becomes darker and darker in color, and at  $200^\circ$  to  $250^\circ$  it is so viscid that the vessel in which it is contained may be turned upside down without danger of its running out. Finally, at  $440^\circ$  it boils and is then converted into a brownish-yellow vapor.

**EXPERIMENT 109.**—Distil about 10 grams of roll sulphur from an ordinary glass retort. Notice the changes above described. Collect the liquid sulphur which passes over in a beaker glass containing cold water.

When molten sulphur solidifies, or when it is deposited from a solution, its particles arrange themselves in regular forms called crystals. But, strange to say, the crystals formed from molten sulphur are entirely different from those deposited from solutions of sulphur. The former are honey-yellow needles. The latter are octahedrons with rhombic base, which is also the form of the sulphur found in nature. A careful examination of the needles shows that the angles which their faces form with one another are not the same as the angles formed by the faces of the octahedrons, and that the crystals are constructed on a different plan. The needles belong to the *monoclinic system* of crystals, and the octahedrons to the *rhombic system*.

**Crystallography.**—Notwithstanding the infinite number of forms assumed by solids in passing from the liquid to the solid state and when deposited from solutions, it has been shown that all can be referred to a very few systems. Usually six systems are adopted. These are :

1. **THE REGULAR SYSTEM.** All the crystals belonging to this system can be referred to three axes of equal length, and at right angles to one another, crossing at the centre. Examples of crystals belonging to this system are the regular octahedron and the cube. The three axes are the imaginary lines which pass through the solid angles of the octahedron. All the other forms of this system may be referred to this octahedron.

2. **THE TETRAGONAL SYSTEM.** In this the forms are referred to three axes at right angles, two of equal length and one differing from the other two. The fundamental forms are the octahedron and prism.

3. **THE HEXAGONAL SYSTEM.** The crystals of this system are referred to four axes,—three of equal length in-

clined at  $60^{\circ}$  to one another, and a fourth at a right angle to them, and either of the same length or different length. The six-sided pyramid and prism are the principal forms.

4. THE RHOMBIC SYSTEM. The crystals belonging to this system have three axes of unequal lengths at right angles to one another.

5. THE MONOCLINIC SYSTEM. In this system the crystals have three axes,—two at right angles to each other, the third at right angles to one and inclined to the other.

6. THE TRICLINIC SYSTEM. The crystals belonging to this system are referred to three axes, all inclined to one another.

The subject of crystallography is one that cannot be made clear in a few words. It requires careful study and much practice in observing forms of crystals. From what has just been said, however, it will be seen that the system of classification of crystals is a simple one. For our present purpose, the fact should be specially emphasized that the crystalline form of a substance is a very definite property, by means of which it may be distinguished from other substances. The fact that a substance crystallizes in the regular system is just as characteristic of that substance as the fact that it boils or melts at a certain point. Thus, we know that ice always melts at  $0^{\circ}$ , and that water solidifies at  $0^{\circ}$ . We should be much surprised to find water solidifying at some other temperature, say  $20^{\circ}$ . Similarly, knowing that sulphur occurs in nature crystallized in forms which belong to the rhombic system, we are naturally surprised to find that, when molten sulphur solidifies, it crystallizes in forms belonging to the monoclinic system. What is perhaps still stranger is the fact that when the

honey-yellow needles are allowed to stand unmolested they spontaneously undergo a change. They become opaque; their color changes; and now, if examined carefully, they are found to consist of minute crystals like those found in nature. It is evident that the arrangement of the particles in the monoclinic crystals of sulphur is not a stable one.

Substances which crystallize in two distinct forms are called *dimorphous*. Carbon crystallizes in two different forms [what are they?], and is hence dimorphous.

**EXPERIMENT 110.**—In a covered sand or Hessian crucible melt about 25 grams of roll sulphur. Let it cool slowly, and when a thin crust has formed on the surface make a hole through this and pour out the liquid part of the sulphur. The inside of the crucible will be found lined with the honey-yellow needles which, as has been stated, belong to the monoclinic system. Take out a few of the crystals and examine them. [Are they brittle or elastic? What is their color? Are they opaque, transparent, or translucent?] Lay the crucible aside, and in the course of a few days again examine the crystals. [What changes, if any, have taken place?]

Sulphur can also be obtained in the amorphous, or uncristallized, condition. That which was collected under water in Experiment 109 will be found to be soft and dough-like. It is amorphous. After a time it becomes brittle.

When separated from a compound which is dissolved in water, it is finely divided, and gives the liquid an appearance suggesting milk.

Sulphur is insoluble in water, slightly soluble in alcohol and ether. It dissolves in the liquid compound of carbon and sulphur known as carbon bisulphide,  $\text{CS}_2$ , and from this solution it is deposited in rhombic crystals.

**EXPERIMENT 111.**—Dissolve 2 to 3 grams roll sulphur in 5 to 10 cc. carbon bisulphide. Put the solution in a shallow vessel, and allow the carbon bisulphide to evaporate by standing in the air. The sulphur will remain behind in the form of crystals.

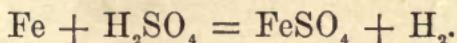
Sulphur combines with oxygen when heated to a sufficiently high temperature. The product is sulphur dioxide,  $\text{SO}_2$ . [Is there any analogy between carbon and sulphur in this respect?] It combines readily with most metals, forming sulphides, which are in some respects analogous to the oxides. Its combination with iron has already been shown in Experiment 10. It also combines with copper, the act being accompanied by light and heat.

**EXPERIMENT 112.**—In a wide test-tube heat some sulphur to boiling. Introduce into it small pieces of copper foil or sheet copper. Or hold a narrow piece of sheet copper so that the end just dips into the boiling sulphur.

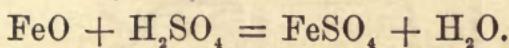
**Hydrogen Sulphide, Sulphuretted Hydrogen,  $\text{H}_2\text{S}$ .**—When hydrogen is passed over highly heated sulphur, the two elements combine to form hydrogen sulphide. [Is there any analogy between this process and the formation of water by the burning of hydrogen?] This compound of sulphur and hydrogen occurs in nature in solution in the so-called sulphur waters, which are met with in many parts of this country as well as in other countries. It also issues from the earth in some places. It is formed by heating organic substances which contain sulphur, just as water is formed by heating organic substances which contain oxygen, and ammonia by heating such as contain nitrogen. It is formed, further, by decomposition of organic substances which contain sulphur, as, for example, the albu-

men of eggs. The odor of rotten eggs is partly due to the formation of hydrogen sulphide.

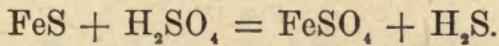
In the laboratory the gas is made most readily by treating a sulphide with an acid. When a metal, as iron, is treated with sulphuric acid, hydrogen is given off and the iron salt of the acid is formed thus :



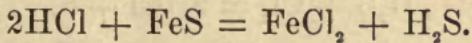
When sulphuric acid acts upon the oxide of iron, hydrogen is given off in combination with oxygen as water, thus :



Finally, when sulphuric acid acts upon iron sulphide, hydrogen is given off in combination with sulphur as hydrogen sulphide, thus :



A similar explanation holds for other acids as well as sulphuric acid. For example, when hydrochloric acid acts upon iron sulphide, the action takes place as represented in the equation



**EXPERIMENT 113.**—Arrange an apparatus as shown in Fig. 47. Put a small handful of the sulphide of iron, FeS, in the flask, and pour dilute sulphuric acid upon it. Pass the evolved gas through a little water contained in the wash cylinder A. Pass some of the gas into water. [What evidence have you that it dissolves?] Collect some by displacement of air. Its specific gravity is 1.178. [Should the vessel be placed with the mouth down or up?]

Set fire to some of the gas contained in a cylinder. If there is free access of air, the sulphur burns to sulphur dioxide and the hydrogen to water.

[What are the products of combustion of marsh gas?]

When treated with chlorine, bromine, or iodine, sulphur

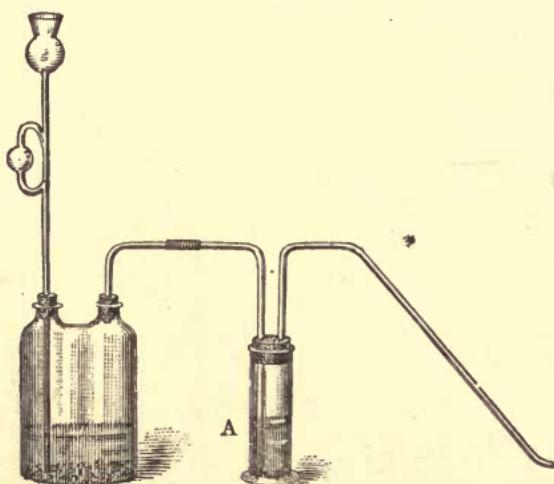
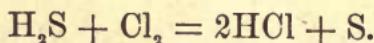


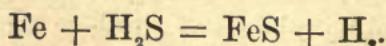
FIG. 47.

is deposited and the hydrogen combines with the other element. Thus, with chlorine the action takes place as represented in the equation



[Does chlorine ever act in a similar way on water? Under what circumstances? What is the peculiarity of the oxygen given off?]

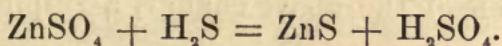
Most metals when heated in the gas are converted into sulphides. Thus, when it is passed over heated iron this reaction takes place:



[What takes place when water vapor is passed over heated iron?]

Many of the sulphides are insoluble in water. Hence, when hydrogen sulphide is passed through solutions containing metals in the forms of soluble salts, the insoluble sulphides are thrown down, or *precipitated*.

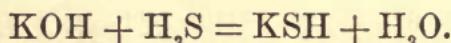
**EXPERIMENT 114.**—Pass hydrogen sulphide successively through solutions containing a little *lead nitrate*, *zinc sulphate*, and *arsenic* prepared by dissolving a little white arsenic, or arsenic trioxide,  $\text{As}_2\text{O}_3$ , in dilute hydrochloric acid. In the vessel containing the lead a black precipitate of lead sulphide will be formed; in the one containing the zinc sulphate there will be formed a white precipitate of zinc sulphide; in the one containing the arsenic, a straw-yellow precipitate of arsenic sulphide will be formed. In all these cases the hydrogen of the sulphur-*ted* hydrogen and the metal of the salt exchange places. For example, in the case of zinc sulphate the reaction takes place thus :



**Chemical Analysis.**—In dealing with chemical substances the first thing we have to determine is their composition, or, in other words, we have to analyze them. For this purpose we must first know the properties of the elements and their general conduct towards chemical substances. To facilitate the process of analysis the mixture to be examined is usually brought into solution and then treated successively with certain substances, the effect being observed in each case. Suppose we had a solution containing most of the metallic elements in the form of salts. If we were to pass through this solution hydrogen sulphide, some of the

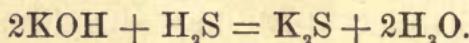
metals would be precipitated in the form of sulphides, while others would remain in solution, as their sulphides are soluble. We then filter off the precipitate and examine it by other methods, and we could also further examine the solution from which the sulphides were precipitated. By adding to this another reagent which will precipitate some of the metals and leave the others in solution, we learn still more in regard to the composition of the substance under examination. Hydrogen sulphide is constantly made use of in the laboratory for the purposes of analysis.

**Hydrosulphides.**—When hydrogen sulphide acts upon hydroxides, the action consists in the formation of *hydrosulphides*. In the case of potassium hydroxide the action takes place thus:

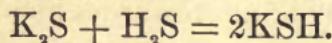


The oxygen and sulphur simply exchange places.

If only half enough hydrogen sulphide is passed into the solution to effect the above change, a sulphide is formed thus:



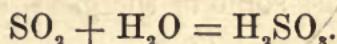
Or if hydrogen sulphide be allowed to act on potassium sulphide, the product is potassium hydrosulphide:



#### COMPOUNDS OF SULPHUR WITH OXYGEN AND WITH HYDROGEN AND OXYGEN.

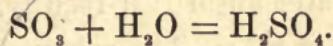
When sulphur burns in the air it forms the dioxide  $\text{SO}_2$ . Under certain conditions the dioxide combines with more

oxygen, forming the trioxide  $\text{SO}_3$ . When sulphur dioxide acts upon water, sulphurous acid is formed:

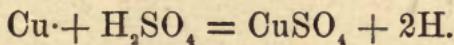


[What analogy is there between the acid thus formed and carbonic acid ?]

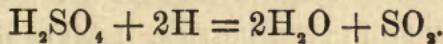
When the trioxide combines with water, sulphuric acid is formed:



**Sulphur Dioxide,  $\text{SO}_2$ .**—This compound is formed by burning sulphur in the air or in oxygen. It issues from volcanoes in large quantities. It is best prepared by treating copper with sulphuric acid. The action does not take place without the aid of heat. We would naturally expect the copper simply to take the place of the hydrogen of the acid:



This is probably the first action that takes place. But the hydrogen acts upon the sulphuric acid, reducing it and forming sulphur dioxide:



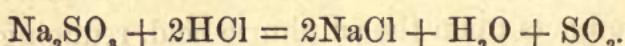
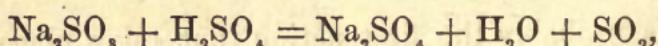
[Compare the action of copper on sulphuric acid with that of copper on nitric acid. What analogy is there between the two cases? What difference?]

**EXPERIMENT 115.**—Put eight or ten pieces of sheet copper, one to two inches long and about half an inch wide, in a 500 cc. flask; pour 15 to 20 cc. concentrated sulphuric acid on it. On heating, sulphur dioxide will be evolved. The

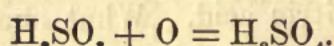
moment the gas begins to come off, lower the flame, and keep it at such a height that the evolution is regular and not too active. Pass some of the gas into a bottle containing water. Collect a vessel full by displacement of air. Its specific gravity is 2.24. See whether the gas will burn or support combustion.

Sulphur dioxide is a colorless gas of an unpleasant, suffocating odor, familiar to every one as that of burning sulphur-matches. Water absorbs it readily.

**Sulphurous Acid,  $H_2SO_3$ .**—The solution in water has acid properties, and probably contains the acid  $H_2SO_3$ . By neutralizing the solution with bases, the *sulphites*, or salts of sulphurous acid, are obtained. The sulphites are analogous to the carbonates in composition, and suffer the same decomposition when treated with acids. When a carbonate is treated with an acid, carbon dioxide is given off. So, also, when a sulphite is treated with an acid, sulphur dioxide is given off:



When a solution of sulphur dioxide is allowed to stand in the air in loosely stoppered bottles, it takes up oxygen, the sulphurous acid being converted into sulphuric acid:



Sulphur dioxide is a good bleaching agent, and is extensively used for the purpose of bleaching wool, silk, straw, paper, etc. In some cases the bleaching is due to the fact that the sulphur dioxide extracts oxygen from the colored

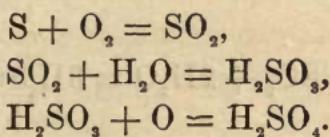
substances, forming colorless products. In other cases the action is more complicated.

**EXPERIMENT 116.**—Burn a little sulphur in a porcelain crucible under a bell jar. Place over the crucible on a tripod some flowers. In the atmosphere of sulphur dioxide the flowers will be bleached.

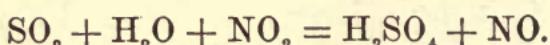
Sulphur dioxide has the power to check fermentation, and is used to preserve liquids which have a tendency to undergo fermentation.

Its principal use is in the manufacture of sulphuric acid. For this purpose it is made in enormous quantities.

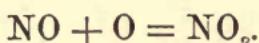
**Sulphuric Acid,  $H_2SO_4$ .**—Sulphuric acid is found in nature in the form of salts, as gypsum, heavy spar, etc. It cannot easily be prepared from its salts, as nitric acid and hydrochloric acids are, and is made exclusively by oxidizing sulphur dioxide in the presence of water, or, in other words, by oxidizing sulphurous acid. The reactions involved in the manufacture of sulphuric acid are:



The last reaction cannot readily be effected directly by the action of the oxygen of the air, but an extremely interesting method has been devised by which the oxygen can be constantly transferred from the air to the sulphurous acid. This method depends partly upon the power of nitric oxide,  $NO$ , to combine directly with air to form nitrogen peroxide,  $NO_2$ . Nitrogen peroxide oxidizes sulphurous acid, and is itself reduced to nitric oxide. If, therefore, sulphur dioxide, water, and nitric oxide be brought together, the first action is represented thus:

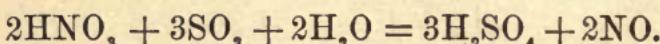


Now, if air be supplied, the nitric oxide will be converted into the peroxide:



The peroxide acting upon a further quantity of sulphur dioxide and water is again reduced, and so on indefinitely. It will thus be seen that, starting with a small quantity of nitric oxide, it should be possible to convert a large quantity of sulphur dioxide into sulphuric acid.

In the manufacture of sulphuric acid, sulphur is burned and the sulphur dioxide conducted into large chambers lined with lead. The reason why lead is used is that sulphuric acid acts upon most other available substances. Instead of starting with nitric oxide, nitric acid is passed into the chambers, and water in the form of steam. The first action between the nitric acid, steam, and sulphur dioxide is this:



From this point we have to deal with sulphur dioxide, water, and nitric oxide, and the chief reactions are those which are described above.

The acid obtained from the chambers contains about 64 per cent of sulphuric acid. It is evaporated in lead pans until it reaches the specific gravity 1.75. As stronger acid acts upon lead, the evaporation is carried on beyond this in platinum or glass. The strong acid thus obtained is the concentrated sulphuric acid of commerce. It is commonly called *oil of vitriol*.

It is an oily liquid, usually somewhat colored by impuri-

ties. The pure acid is a colorless liquid at ordinary temperatures. When cooled down it forms crystals. It is a very strong acid, decomposing the salts of most other acids, setting the acids free, and appropriating the metals. We have already had illustrations of this power in the liberation of nitric and hydrochloric acids from their salts by treatment with sulphuric acid.

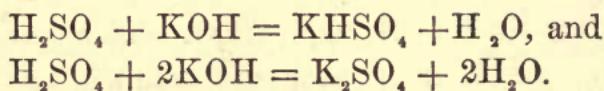
[Give the equations representing the action which takes place when common salt and potassium nitrate are treated with sulphuric acid.]

Sulphuric acid has a very strong tendency to absorb water, and to form compounds with it. The simplest of these is the hydrate  $H_2SO_4 + H_2O$ . This is a crystallized substance which melts at a low temperature ( $7.5^\circ$ ). In consequence of the formation of these hydrates, a great deal of heat is evolved when sulphuric acid is mixed with water. This fact has been repeatedly illustrated in experiments already performed; and the necessity for precaution in mixing the two liquids has been emphasized. The acid acts upon organic substances containing hydrogen and oxygen, and extracts these elements in the proportions to form water. If a piece of wood be put in the acid it is charred, in consequence of the abstraction of hydrogen and oxygen. [How is wood usually charred in the preparation of charcoal? Is there any analogy between the preparation of charcoal in the ordinary way and by the action of sulphuric acid?] Wounds caused by sulphuric acid are painful and difficult to heal.

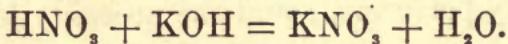
The acid is used for the purpose of drying gases upon which it does not act. [Can it be used for drying ammonia?]

**Monobasic and Dibasic Acids.**—Sulphuric acid differs

markedly from nitric and hydrochloric acids in one respect. It has the power to form two different salts with the same metal, in one of which there is twice as much metal as in the other. If to a given quantity of sulphuric acid there be added only half the quantity of caustic potash required to neutralize it, a salt is formed which crystallizes. It has the composition represented by the formula  $\text{KHSO}_4$ . If nitric acid be treated in the same way, only half the acid is acted on, and this forms ordinary potassium nitrate,  $\text{KNO}_3$ , the rest of the acid being left unacted upon. In the case of sulphuric acid two reactions are possible, viz.:



In the case of nitric acid, only one reaction seems to be possible :



Acids which, like sulphuric acid, have the power to form two salts with the same metal are called *dibasic acids*. Acids which, like nitric acid, have the power to form only one salt with the same metal are called *monobasic acids*. This power is connected with the number of replaceable hydrogen atoms contained in the molecule of the acids. An acid containing two replaceable hydrogen atoms in its molecule is dibasic; one containing one replaceable hydrogen atom in its molecule is monobasic.

**Acid, Neutral, and Normal Salts.**—A dibasic acid yields two classes of salts: (1) those in which all the hydrogen is replaced, and (2) those in which half the hydrogen is replaced by metal. The former are called *normal salts*, the

latter *acid salts*. Normal salts are generally neutral, and are sometimes called *neutral salts*.

**Other Acids Containing Sulphur.**—Besides sulphurous and sulphuric acids, sulphur forms several other acids. These cannot be considered here. Their names and formulas are as follows:

Hydrosulphurous acid,  $H_2SO_2$ ; Pyrosulphuric acid,  $H_2S_2O_7$ ; Thiosulphuric acid,  $H_2S_2O_3$ ; Trithionic acid,  $H_2S_3O_6$ ; Dithionic acid,  $H_2S_2O_6$ ; Tetrathionic acid,  $H_2S_4O_6$ .

The sodium salt of thiosulphuric acid,  $Na_2S_2O_3$ , commonly called *sodium hyposulphite*, is used in photography. *Pyrosulphuric acid*, or *fuming sulphuric acid*, breaks up into sulphuric acid and sulphur trioxide,  $H_2S_2O_7 = H_2SO_4 + SO_3$ , and is a powerful reagent for some purposes.

**Carbon Bisulphide,  $CS_2$ .**—Sulphur forms with carbon a compound known as carbon bisulphide, which has the composition represented by the formula  $CS_2$ . It is made by bringing carbon and sulphur together at high temperatures. It is a liquid which boils at  $47^\circ$ . That it dissolves sulphur has already been seen (see Experiments 9 and 111). It also dissolves many other substances.

**Selenium and Tellurium and their Compounds.**—These elements are rarely met with. In general, their properties are very similar to those of sulphur, and they form compounds analogous to the principal compounds of sulphur. They combine with hydrogen, forming gases which have bad odors—much worse than that of hydrogen sulphide. They burn in oxygen, forming oxides,  $SeO_2$  and  $TeO_2$ . Corresponding to these oxides there are acids,  $H_2SeO_4$  and  $H_2TeO_4$ , the analogues of sulphurous acid, and  $H_2SeO_4$  and

$\text{H}_2\text{TeO}_4$ , the analogues of sulphuric acid. The compounds with hydrogen are less stable than hydrogen sulphide.

The atomic weights of the three elements of the sulphur family bear a simple relation to one another, like that already noticed between the atomic weights of the members of the bromine family. We have sulphur, 32; selenium, 79; tellurium, 125. The atomic weight of selenium is nearly the mean of the atomic weights of sulphur and tellurium:

$$\frac{32 + 125}{2} = 78.5$$

**Points of Resemblance between Oxygen and the Members of the Sulphur Family.**—Between the elements oxygen and sulphur there is very little resemblance, but the compounds of the two elements present many points of analogy. This is seen particularly in the compounds which they form with hydrogen and with the metals. Water and hydrogen sulphide are analogous in composition and in their decompositions. This is also markedly true of the metallic oxides and sulphides; and of the hydroxides and hydrosulphides. On the other hand, oxygen is unique in many respects, and is certainly not nearly so closely related to sulphur as selenium and tellurium are.

## CHAPTER XV.

### THE NITROGEN FAMILY: NITROGEN, PHOSPHORUS, ARSENIC, AND ANTIMONY.

BETWEEN the element nitrogen and the other elements which are included in this family there is but little resemblance. Nitrogen, as we have seen, is a very inactive element. Phosphorus, on the other hand, is one of the most active. Nitrogen does not combine directly with oxygen. Phosphorus combines with oxygen even at ordinary temperatures, while at the burning temperature the combination takes place violently. The elements arsenic and antimony resemble each other in many respects, and are also allied to phosphorus. On studying the compounds which all the members of the family form, we recognize clearly that they are closely related.

**Phosphorus, P (At. Wt. 31).**—This element occurs in nature in the form of phosphates, or salts of phosphoric acid. The chief of these is calcium phosphate, which is the principal constituent of the minerals *phosphorite* and *apatite* and of the ashes of bones.

It is prepared from bone-ash. This is first treated with sulphuric acid. The acid converts it into a compound, which, when mixed with charcoal and heated, is reduced, yielding free phosphorus. The phosphorus thus obtained is cast into sticks under water, and preserved under water.

It is colorless or slightly yellow and translucent. At or-

dinary temperatures it can be cut like wax, but it becomes hard and brittle at lower temperatures. It melts at a low temperature ( $44^{\circ}$ ) and boils at  $290^{\circ}$ . Unless carefully protected from the light, its appearance changes. It becomes opaque and darker in color, and finally dark red. This change can be hastened by heating the phosphorus in a sealed tube to a temperature of about  $250^{\circ}$ .

It is insoluble in water, but soluble in carbon bisulphide. In contact with the air it gives off fumes which emit a pale light visible in a dark room. It takes fire when rubbed or cut, and must hence be handled with great care. It should always be cut under water, and never held in the hand. It not only combines with oxygen easily, but with other elements, such as chlorine, bromine, and iodine, the action in each case being accompanied by an evolution of heat and light. The combination of phosphorus with oxygen has already been seen. Its conduct towards iodine can be shown by a very simple experiment.

**EXPERIMENT 117.**—Bring together in a porcelain crucible or evaporating-dish a little phosphorus and iodine. It will be seen that simple contact is sufficient to cause the two substances to act upon each other. Direct combination takes place, and the action is accompanied by light and heat.

Phosphorus is very poisonous. It is used in the manufacture of matches.

**Red Phosphorus.**—The red substance formed when ordinary phosphorus is left in the light, or heated without access of air, is a second variety of phosphorus known as red phosphorus. This differs from ordinary phosphorus as much as graphite differs from the diamond. Ordinary phosphorus is very active, combining readily with oxy-

gen; it is soluble in carbon bisulphide; and is poisonous. Red phosphorus, on the other hand, is inactive. It does not change in the air, and requires to be heated to a comparatively high temperature before it will combine with oxygen; it is insoluble in carbon bisulphide, and is not poisonous. Red phosphorus is converted into the ordinary variety by heating it to about 300°.

The cause of the great difference in the properties of the two varieties of phosphorus is not known.

There are some other modifications of phosphorus, but they are rarely met with.

**Phosphine, Phosphuretted Hydrogen, PH<sub>3</sub>.**—The chief compound of phosphorus and hydrogen is phosphine, PH<sub>3</sub>. It is made by dissolving phosphorus in caustic potash or soda. The reaction which takes place is not altogether simple, and need not be explained at present. The points of chief interest in regard to the substance are: (1) its composition, PH<sub>3</sub>, which is analogous to that of ammonia, NH<sub>3</sub>; (2) its power to combine with some acids as ammonia does, forming unstable phosphonium salts analogous to the ammonium salts; and (3) its power to take fire when brought in contact with the air.

It has a disagreeable odor.

**EXPERIMENT 118.**—Arrange an apparatus as shown in Fig. 48. In the flask *B* put about 5 grams caustic potash, dissolved in 10–15 cc. water, and add a few small pieces of phosphorus the size of a pea. Pass hydrogen for some time through the apparatus from the generating-flask *A* until all the air is displaced; then disconnect at *D*, leaving the rubber tube, closed by the pinch-cock, on the tube which enters the flask. Gently heat the contents of the retort, when gradually a gas will be evolved and escape through the water in *C*. As each

bubble comes in contact with the air it takes fire, and the products of combustion arrange themselves in rings which become larger as they rise. They are extremely beautiful, particularly if the air of the room is quiet. Both the

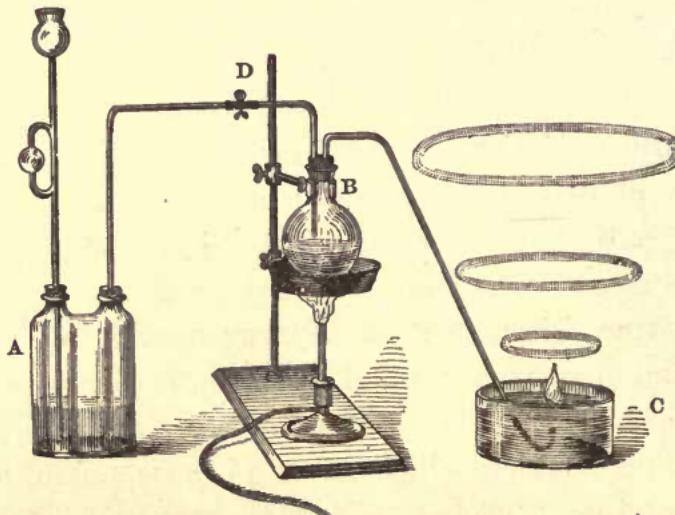
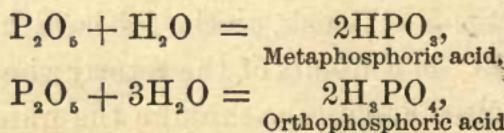


FIG. 48.

phosphorus and the hydrogen combine with oxygen in the act of burning.

The spontaneous inflammability of phosphine has been found to be due to the presence of a small quantity of another compound of phosphorus and hydrogen which is formed by the action of phosphorus on caustic potash.

**Compounds of Phosphorus with Oxygen and with Hydrogen and Oxygen.**—The product formed by the combination of phosphorus and oxygen has the composition expressed by the formula  $P_2O_5$ . This combines with water in different proportions, forming two distinct acids, known as *metaphosphoric* and *orthophosphoric acids*:



**Orthophosphoric or ordinary phosphoric acid,  $H_3PO_4$ ,** is the principal compound of phosphorus. It is the final product of the action of air and moisture on phosphorus. As has been stated, it occurs in nature as the calcium salt in phosporite and apatite. This salt is also the chief constituent of bone-ash.

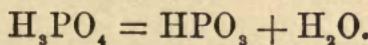
It can be made by treating bone-ash with sulphuric acid, or by oxidizing phosphorus.

It is a solid crystallized substance.

Phosphoric acid has the power of forming three distinct salts with the same metal. It is hence called *tribasic*. With sodium, for example, it forms the three salts  $Na_3PO_4$ ,  $Na_2HPO_4$ , and  $NaH_2PO_4$ . Its normal calcium salt—that is to say, the one in which all the three acid hydrogen atoms are replaced by calcium—has the formula  $Ca_3(PO_4)_2$ , three bivalent calcium atoms replacing six atoms of hydrogen.

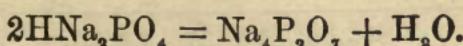
[Write the equation expressing the action which takes place when sulphuric acid decomposes normal calcium phosphate, forming calcium sulphate and phosphoric acid.]

When phosphoric acid is heated to a sufficiently high temperature, it loses hydrogen and oxygen in the form of water and yields *metaphosphoric acid*:

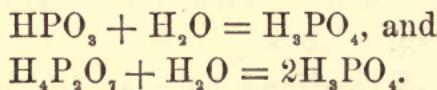


Metaphosphoric acid is the substance found in commerce under the name of *glacial phosphoric acid*. It is made by evaporating solutions of phosphoric acid down to dryness and heating the residue.

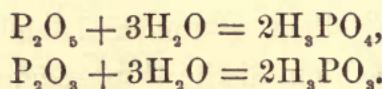
When a salt, like ordinary sodium phosphate,  $HNa_2PO_4$ , is heated, it loses water and yields a salt of *pyrophosphoric acid*:



It will thus be seen that ordinary phosphoric acid by losing water yields pyrophosphoric acid,  $H_4P_2O_7$ , and metaphosphoric acid,  $HPO_3$ . Both these acids take up water and are reconverted into ordinary phosphoric acid :

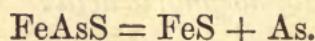


**Phosphorous Acid,  $H_3PO_3$ .**—This acid is formed by allowing moist air to act on phosphorus. There is an oxide,  $P_2O_5$ , which bears to the acid the same relation that phosphorus pentoxide bears to phosphoric acid :

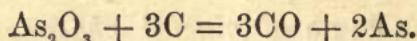


**Arsenic and its Compounds.**—Arsenic\* occurs in nature in combination with metals—as, for example, iron, copper, cobalt, nickel, etc.—and in combination with oxygen, as the trioxide  $As_2O_3$ .

It is generally obtained by heating arsenical pyrites,  $FeAsS$ , when the arsenic separates from the iron and sulphur :



It is also made by reducing arsenic trioxide :



It has a metallic lustre. When heated to quite a high temperature in the air it takes fire, and burns with a bluish flame, giving off a smoke which has the odor of garlic and is poisonous.

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\* Symbol, As. At. wt. 75.

It combines directly with most elements. In the elementary form it is not poisonous, but when oxidized it becomes so.

**Arsine, Arseniuretted Hydrogen, AsH<sub>3</sub>.**—This compound is analogous to ammonia and phosphine. It is made by the action of nascent hydrogen [what is nascent hydrogen?] on the compounds of arsenic with oxygen, as when these compounds are brought into a vessel containing zinc and sulphuric acid.

**EXPERIMENT 119.**—Arrange an apparatus as shown in Fig. 49. Put some granulated zinc in the Wolff flask and

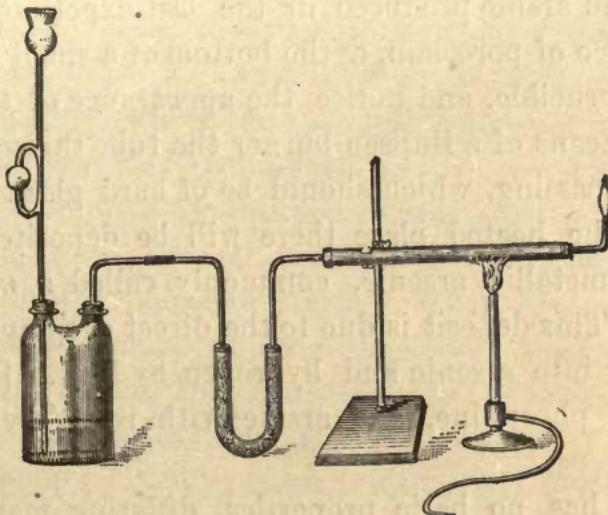


FIG. 49.

pour dilute sulphuric acid on it. When the air is all out of the vessel and the hydrogen is lighted, add slowly a little of a solution of arsenic trioxide, As<sub>2</sub>O<sub>3</sub>, in dilute hydrochloric acid. The appearance of the flame will soon change, becoming paler, with a slightly bluish tint, and giving off white fumes. (See Experiment 120.)

Arsine is a colorless gas. It is very poisonous and has an unpleasant odor. When lighted it burns with a bluish-

white flame, forming arsenic trioxide and water. It is very unstable, breaking up into arsenic and hydrogen when heated. When a cold object, as a piece of porcelain, is brought into the flame of burning arsine, the arsenic is deposited in the form of a dark spot. This fact is taken advantage of for the purpose of detecting the presence of arsenic. It is extensively used in examining the stomach and other viscera of human beings in cases of suspected poisoning. It is known as *Marsh's test*, having been introduced by a chemist by the name of Marsh.

**EXPERIMENT 120.**—Into the flame of the burning hydrogen and arsine produced in the last experiment introduce a piece of porcelain, as the bottom of a small porcelain dish or a crucible, and notice the appearance of the spots. Heat by means of a Bunsen burner the tube through which the gas is passing, which should be of hard glass. Just in front of the heated place there will be deposited a thin layer of metallic arsenic, commonly called a *mirror of arsenic*. This deposit is due to the direct decomposition of the arsine into arsenic and hydrogen by heat. [Compare ammonia, phosphine, and arsine with reference to their stability.]

Arsine has no basic properties, differing markedly in this respect from ammonia. Phosphine, as has been stated, has weak basic properties.

**Arsenic Trioxide, As<sub>2</sub>O<sub>3</sub>.**—When arsenic is burned in the air or in oxygen it forms the trioxide. [Compare with phosphorus in this respect.] This substance, which is generally called arsenic, is made by heating compounds of arsenic and metals in contact with the air. Under these circumstances, both the metal and the arsenic are oxidized, and the oxide of arsenic, being volatile, passes off and is

condensed and collected in large chambers of mason-work.

It is a colorless, amorphous, glassy mass. It is difficultly soluble in water, more easily in hydrochoric acid. It has a weak, disagreeably sweet taste, and acts very poisonously. It is probably more frequently used as a poison than any other substance. Minute quantities can be detected by the chemist with absolute certainty.

The oxide is easily reduced by means of carbon.

**EXPERIMENT 121.**—Mix together about equal small quantities of arsenic trioxide and finely powdered charcoal. Heat the mixture in a small dry tube of hard glass, closed at one end. The arsenic which is set free will be deposited on the walls of the tube in the form of a mirror, like that obtained in Experiment 120.

Arsenic forms with oxygen and hydrogen an acid of the formula  $H_3AsO_4$ , known as *arsenic acid*, which is analogous to orthophosphoric acid. When heated, it undergoes changes similar to those considered in connection with phosphoric acid, the products being *metarsenic acid*,  $HAsO_3$ , and *pyroarsenic acid*,  $H_4As_2O_7$ .

When arsenic trioxide is treated with bases in solution, salts of *arsenious acid*, or the *arsenites*, are formed. The formula of the potassium salt is  $K_3AsO_3$ . The acid  $H_3AsO_3$  differs from arsenic acid,  $H_3AsO_4$ , by one atom of oxygen in the molecule.

**Antimony\*** occurs most frequently in combination with sulphur as the sulphide  $Sb_2S_3$ . It is a silver-white, metallic-looking substance. At ordinary temperature it is not changed by contact with the air; but when heated to

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\* Symbol, Sb. At. wt. 120.

a sufficiently high temperature in the air it takes fire and burns, forming the white oxide.

**EXPERIMENT 122.**—Heat a small piece of antimony on charcoal by means of the blow-pipe. Notice the formation of the white coating on the charcoal around the place where the substance burned. [What difference is there between the conduct of antimony and arsenic before the blow-pipe?] It would be well for the teacher to give the student a small piece of arsenic and another of antimony, and ask him to determine by means of the blow-pipe which is the arsenic and which is the antimony.

**Stibine, Antimoniuretted Hydrogen, SbH<sub>3</sub>.**—This compound is made by the same method as that described under arsine.

**EXPERIMENT 123.**—Make some stibine, using a solution of tartar emetic which contains antimony.

Its properties are very much like those of arsine. It burns with a similar flame and is decomposed in the same way.

**EXPERIMENT 124.**—Introduce a piece of porcelain in the flame and notice the deposit or antimony spot. It is darker and more smoky than the arsenic spot. There are other differences in properties, but they need not be considered here.

Antimony forms acids resembling phosphoric, metaphosphoric, and pyrophosphoric acids.

**Antimony as a Base-forming Element.**—Antimony not only forms acids with hydrogen and oxygen, but it also forms bases. These bases neutralize acids and form salts in which the hydrogen of the acids is replaced by antimony. Some of these salts are rather complicated in composition, and it would lead too far to discuss them here. It is suffi-

cient for our present purpose to recognize the important fact that one and the same element has the power to form acids and bases.

Antimony, however, is not the only element thus far considered which has this double power. The compounds of nitrogen with hydrogen and oxygen have, in general, acid properties, but ammonia has strongly basic properties. We see, therefore, that when nitrogen is combined with hydrogen the product has basic properties, while when combined with hydrogen and oxygen in forms in which the oxygen is in excess the products are acids. The same is true to a slight extent of phosphorus.

At the same time, neither the element nitrogen nor the element phosphorus itself has the power to replace the hydrogen of acids, and this power antimony has.

There are three rare elements which in their chemical conduct resemble the members of the nitrogen family. These are *vanadium*, *columbium*, and *tantalum*. It would be unprofitable to undertake their study at this stage.

**General Remarks on the Characteristics of the Nitrogen Family.**—The resemblance between nitrogen and phosphorus is seen particularly in the compounds ammonia and phosphine. Between the oxides of nitrogen and of phosphorus the resemblance is not striking. There are two oxides of nitrogen,—the trioxide,  $N_2O_3$ , and the pentoxide,  $N_2O_5$ , which in composition correspond to the two oxides of phosphorus,  $P_2O_3$  and  $P_2O_5$ . But while the pentoxide of phosphorus is the most common oxide of this element, the pentoxide of nitrogen is obtained with greater difficulty than any of the other oxides of nitrogen. There are no compounds of phosphorus analogous to the three principal oxides of nitrogen,—nitrous oxide,  $N_2O$ ; nitric oxide,  $NO$ ,

and nitrogen peroxide,  $\text{NO}_2$ . There is no acid of phosphorus corresponding to nitrous acid,  $\text{HNO}_2$ , and there are no compounds of nitrogen analogous to phosphoric acid,  $\text{H}_3\text{PO}_4$ , and pyrophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_7$ . Nitric acid,  $\text{HNO}_3$ , and metaphosphoric acid,  $\text{HPO}_3$ , have analogous compositions.

The resemblance between phosphorus, arsenic, and antimony is much more striking than that between nitrogen and phosphorus. This resemblance has already been noticed in the acids formed by the three elements, and in their hydrogen compounds,  $\text{PH}_3$ ,  $\text{AsH}_3$ , and  $\text{SbH}_3$ , all of which are analogous to ammonia. The same resemblance is seen in their oxides,  $\text{P}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{As}_2\text{O}_3$ ,  $\text{As}_2\text{O}_5$ , and  $\text{Sb}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_5$ . Their compounds with chlorine and the other members of the chlorine family are also strikingly similar.

The elements of the nitrogen family are *trivalent* in some compounds, as in  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$ ,  $\text{PCl}_3$ ,  $\text{AsCl}_3$ , etc.; and *quinquivalent* in others, as in  $\text{NH}_4\text{Cl}$ , in which the nitrogen is believed to hold in combination four atoms of hydrogen and one atom of chlorine; in  $\text{PCl}_5$ , etc., etc.

The atomic weights are  $\text{N} = 14$ ;  $\text{P} = 31$ ;  $\text{As} = 75$ ;  $\text{Sb} = 120$ . These figures do not all bear simple relations to one another, but between the atomic weights of phosphorus, arsenic, and antimony there exists a relation similar to that already noticed between the atomic weights of chlorine, bromine, and iodine, and sulphur, selenium, and tellurium. We have  $\text{P} = 31$ ,  $\text{Sb} = 120$ , and  $\text{As} = 75$ :

$$\frac{31 + 120}{2} = 75.5.$$

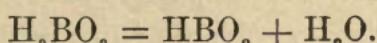
**Boron, B (At. Wt. 10.9).**—Boron may conveniently be considered in connection with the nitrogen family, as some

of its properties suggest those of the members of the family. At the same time, it presents peculiarities which distinguish it from these elements. Boron occurs in nature in the form of boric acid, or as salts of this acid, particularly the sodium salt, or *borax*. It is prepared by treating the oxide,  $B_2O_3$ , at a very high temperature with sodium or aluminum. Under proper conditions it is obtained in the form of crystals which are almost as hard as diamonds.

At a red heat uncrySTALLIZED boron combines with nitrogen very readily. The crystallized variety can be heated to a high temperature in the air without changing. These properties distinguish boron from the members of the nitrogen family, all of which, with the exception of nitrogen, combine with oxygen. Boron combines with chlorine, forming the chloride  $BCl_3$ , analogous to the chlorides of phosphorus and arsenic,  $PCl_3$  and  $AsCl_3$ .

**Boric Acid,  $H_3BO_3$ .**—The chief compound of boron is boric acid. It occurs in nature in large quantities, issuing from the earth with water vapor in some localities, particularly in Tuscany. The jets of steam charged with boric acid, which are called *suffioni*, are conducted into tanks of water, in which the acid condenses. The solution is evaporated by means of the heat of the natural steam-jets, and finally the acid crystallizes out. The acid is also obtained from a natural magnesium salt called *boracite*, and from *borax*, which is a sodium salt.

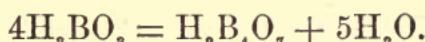
When heated to  $100^\circ$ , boric acid loses water and is converted into *metaboric acid*,  $HBO_2$ :



[What is the analogous change of phosphoric acid?]

The acid thus obtained is analogous to nitrous acid in composition.

When heated higher, a larger proportion of water is given off, and an acid of the formula  $H_2B_4O_7$ , or *tetraboric acid*, is left behind. This is the form of boric acid from which borax is derived. The formula of borax is  $Na_2B_4O_7 + 10H_2O$ . The relation between tetraboric acid and normal boric acid is shown by the equation



Heated to a still higher temperature, boric acid loses all its hydrogen in the form of water, and leaves behind *boron trioxide*, or *boric anhydride*,  $B_2O_3$ . [What is the significance of the name boric anhydride?]

When a solution of borax is treated with sulphuric acid, boric acid is set free, and crystallizes out if the solution is concentrated enough.

**EXPERIMENT 125.**—Make a hot solution of 30 grams crystallized borax in 120 cc. water. Add *slowly* 10 grams concentrated sulphuric acid. On cooling, the boric acid will crystallize out. [What evidence have you that the substance which crystallizes out of the solution is not borax?] Try the solubility in alcohol of specimens of each. [Is there any difference?] Treat a few crystals of borax with about 10 cc. alcohol; pour off the alcohol and set fire to it. Treat a few crystals of the boric acid in the same way. [What difference do you observe?]

**Boric Anhydride,  $B_2O_3$** , when heated, melts and forms a clear glass. This has the power to dissolve many substances which ordinary solvents will not dissolve, and some of the solutions thus formed are colored. This fact is taken advantage of in the laboratory for the purpose of

detecting the presence of those substances which form colored solutions. The method of work consists in melting a little boric acid or borax in a loop of platinum wire, and then bringing a minute particle of the substance to be examined in contact with the glass bead thus formed. When heated before the blow-pipe it will generally dissolve. By holding the bead in the oxidizing flame of the blow-pipe the substance in solution is frequently oxidized, and by holding it in the reducing flame it is frequently reduced. Changes of color may thus be produced which will aid us in determining what substance we have to deal with. This method is valuable for the purposes of analysis.

When an alcoholic solution of boric acid is lighted, it burns with a green flame. The salts of boric acid do not color the alcohol flame. [What evidence have you had of the truth of this statement?]

Boron is trivalent in most of its compounds, as in the chloride,  $\text{BCl}_3$ .

## CHAPTER XVI.

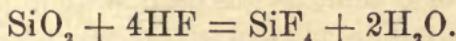
### THE CARBON FAMILY: CARBON AND SILICON.

**Silicon, Si (At. Wt. 28).**—We have already learned how important a rôle carbon plays in animate nature. It is interesting to note that silicon, which in some respects resembles carbon from a chemical standpoint, is one of the most important constituents of the mineral or inorganic parts of the earth. It occurs chiefly in the form of the oxide,  $\text{SiO}_2$ , commonly called silica, or silicon dioxide; and in combination with oxygen and several of the common metals, particularly with sodium, potassium, aluminium, and calcium, in the form of the silicates. Next to oxygen, silicon is the most abundant element in nature. There are extensive mountain-ranges consisting almost entirely of silicon dioxide,  $\text{SiO}_2$ , in the form known as *quartz* or *quartzite*. Other ranges are made up of silicates, which are compounds formed by a combination of silicon dioxide and bases. The clay of valleys, river-beds, etc., also contains silicon in large quantity, while the sand found so abundantly at the sea-shore is mostly silicon dioxide,  $\text{SiO}_2$ .

Silicon is never found in the free state, and it is an extremely difficult thing to decompose the oxide,  $\text{SiO}_2$ , in such a way as to get the element, though it can be accomplished by heating the oxide with potassium. Under proper conditions silicon can be obtained in the form of crystals which have a gray color and are harder than

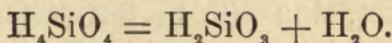
glass. It is not acted upon by the strongest acids, nor when heated in a current of oxygen.

With hydrogen silicon forms a gaseous compound of the formula  $\text{SiH}_4$ ; it combines with chlorine, forming  $\text{SiCl}_4$ , and with fluorine, forming  $\text{SiF}_4$ . The fluoride has already been referred to in connection with the action of hydrofluoric acid on silicates. We have seen that hydrofluoric acid dissolves silicates—as, for example, glass—in consequence of the action of the acid on silicon dioxide, which is represented thus:

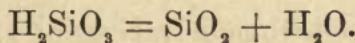


The silicon fluoride passes off in the form of gas.

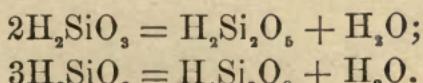
**Silicic Acid.**—There are several varieties of silicic acid, all of which are, however, derived from an acid of the formula  $\text{H}_4\text{SiO}_4$ , or normal silicic acid. When this is set free from its salts, it loses water, and is changed to ordinary silicic acid,  $\text{H}_2\text{SiO}_3$ :



When heated, this second form of silicic acid is converted into the dioxide  $\text{SiO}_2$ :



Most of the ordinary silicates are derived from the acid of the formula  $\text{H}_2\text{SiO}_3$ . [What is the formula of carbonic acid? Under what circumstances does carbonic acid break up into carbon dioxide and water?] Other silicic acids are obtained by heating ordinary silicic acid. Thus, under the proper conditions an acid of the formula  $\text{H}_2\text{Si}_2\text{O}_5$ , and one of the formula  $\text{H}_4\text{Si}_3\text{O}_8$ , can be obtained:



These are called *polysilicic acids*. Some of these are found in nature. Opal is the best known example.

**Silicon Dioxide, Silicic Anhydride,  $\text{SiO}_2$ .** — As already stated, this substance occurs very abundantly in nature and in many different forms. *Quartz*, or *rock crystal*, is pure crystallized silicon dioxide; *quartzite* is a coarser-grained substance made up of small crystals of quartz, usually colored. Agate, amethyst, and carnelian are varieties of quartz colored by foreign substances.

Silicon dioxide is insoluble in water and acids. It is soluble in hydrofluoric acid, as has been stated. *Glass* is made up of salts of silicic acid, usually of the sodium or potassium salts and calcium salts.

**Comparison of Carbon and Silicon.**—The two elements of this family resemble each other in the composition of some of their simplest compounds, as carbon dioxide,  $\text{CO}_2$ , and silicon dioxide,  $\text{SiO}_2$ ; carbonic acid,  $\text{H}_2\text{CO}_3$ , and silicic acid,  $\text{H}_2\text{SiO}_3$ ; marsh gas,  $\text{CH}_4$ , and silicon hydride,  $\text{SiH}_4$ ; carbon tetrachloride,  $\text{CCl}_4$ , and silicon tetrachloride,  $\text{SiCl}_4$ . On the other hand, they present marked points of difference. Each yields a large number of derivatives, but the derivatives of carbon bear to the element relations entirely different from those which the derivatives of silicon bear to this element. The compounds of carbon can all be shown to be derived from the hydrocarbons; that is to say, they may be regarded as formed from the hydrocarbons by a comparatively simple set of changes [what are the hydrocarbons?], while most of the compounds containing silicon are derivatives of silicic acid.

## CHAPTER XVII.

### BASE-FORMING ELEMENTS.—GENERAL CONSIDERATIONS.

At the end of Chapter XII. is this sentence: "After the acid-forming elements have been considered, the base-forming elements will be taken up in a similar way; but, as will be seen, the chemistry of the acid-forming elements exhibits more variety, and is hence better adapted to the illustration of the general principles of the science than that of the base-forming elements, so that the latter need not be considered as fully."

The significance of the name base-forming elements has been stated. It is simply this: that the compounds of these elements with hydrogen and oxygen are bases, or, in other words, have the power to neutralize acids and form salts. But the distinction between acid-forming and base-forming elements is not a sharp one, for the reason that there are some elements which occupy an intermediate position, forming both acids and bases. One example of this kind already considered is antimony, and the reason why it was considered as a member of the nitrogen family is that it is unquestionably closely related to arsenic, which is strictly an acid-forming element. A close study will show that those elements which have the power to form both acids and bases are related to one of the four families already considered. There are, thus, certain elements which

show some resemblance to the members of the chlorine family, but nevertheless act principally as base-formers; so, too, there are certain elements which resemble the members of the sulphur family, but which generally form bases. In a similar way, there are base-forming analogues of the nitrogen and carbon families. Those elements which always act as base-formers have no analogues among the acid-forming elements.

The order in which the base-forming elements will be taken up is the following:

1. The *Potassium Family*, consisting of lithium, sodium, potassium, rubidium, and cæsium.
2. The *Calcium Family*, consisting of glucinum, calcium, barium, and strontium.
3. The *Magnesium Family*, consisting of magnesium, zinc, and cadmium.
4. The *Silver Family*, consisting of silver, copper, and mercury.
5. The *Aluminium Family*, of which aluminium is the only well-known member. Allied to it are the rare elements gallium, indium, thallium, scandium, yttrium, lanthanum, and ytterbium.
6. The *Iron Family*, consisting of iron, cobalt, and nickel.
7. The *Manganese Family*, of which manganese is the only representative. There are some points of resemblance between manganese and the members of the chlorine family.
8. The *Chromium Family*, consisting of chromium, molybdenum, and tungsten. The members of this family show some analogy to the members of the sulphur family, as will be pointed out when chromium is considered.
9. The *Bismuth Family*, of which bismuth is the only

representative. There are some points of resemblance between bismuth and the members of the nitrogen family.

10. The *Lead Family*, consisting of the common elements lead and tin, and the rare elements titanium, zirconium, cerium, and thorium.

11. The *Palladium Family*, consisting of palladium, ruthenium, and rhodium.

12. The *Platinum Family*, consisting of osmium, iridium, platinum, and gold.

It will be seen at once that there are many more base-forming than acid-forming elements, and it is a serious undertaking to become thoroughly acquainted with all the elements included under this head. In order to get a general knowledge of the principles of chemistry, however, it is not necessary to study all these elements. The chemist must, of course, familiarize himself to some extent with all of them, and those who continue the study of chemistry hereafter will have abundant opportunity to study them in detail. For the present it will be best to confine our attention to a few of the representative elements included in the above list. A knowledge of these will put us in a position to study the others without serious difficulty, should occasion demand.

**Metallic Properties.** — It is customary to divide the chemical elements into two classes,—the *metals* and the *non-metals*. This classification was originally based upon differences in the physical properties of the elements, the name metal being applied to those elements which have what is known as a metallic lustre, are opaque, and are good conductors of heat and electricity. All those elements which do not have these properties are called non-metals. Gradually the name metal came to signify an element which

has the power to replace the hydrogen of acids and form salts, and the name non-metal to signify an element which has not this power. This classification is in reality about the same as that which is made use of in this book. It thus appears that, in general, elements which have similar physical properties have also similar chemical properties.

**Classes of Metal Derivatives.**—As the metals or base-forming elements all combine with oxygen, sulphur, chlorine, and hydrogen and oxygen, and also form salts with all acids, it follows that under the head of each one there must be a large number of compounds. A thorough study of each metal would include the following subjects:

1. *Its Occurrence in Nature.*—Under this head we would become acquainted with those natural compounds of the metals known as *minerals*. Those minerals from which the metals are extracted for practical purposes are called *ores*.

2. *Extraction of the Metals from their Ores.*—The detailed study of this subject is the object of *metallurgy*.

3. *The Properties of Metals as such.*—As we shall find, metals differ very markedly from one another. Some are light, floating on water, as lithium, sodium, etc.; some are extremely heavy, as lead, platinum, etc. Some combine with oxygen with great energy; others form very weak compounds with oxygen. Some form strong bases, others form weak bases.

4. *The Compounds of the Metals.*—These may be conveniently classified as :

a. Compounds with chlorine, bromine, and iodine; or the *chlorides*, *bromides*, and *iodides*.

b. Compounds with oxygen and with oxygen and hydrogen; or the *oxides* and *hydroxides*.

c. Compounds with sulphur and with sulphur and hydrogen ; or the *sulphides* and *hydrosulphides*.

d. Compounds with nitric and nitrous acids ; or the *nitrates* and *nitrites*.

e. Compounds with the acids of chlorine ; or the *chlorates*, *chlorites*, etc.

f. Compounds with sulphuric and sulphurous acids ; or the *sulphates* and *sulphites*.

g. Compounds with carbonic acid ; or the *carbonates*.

h. Compounds with phosphoric acid and the analogous acids of arsenic and antimony ; or the *phosphates*, *arsenates*, etc.

i. Compounds with silicic acid ; or the *silicates*.

j. Compounds with boric acid ; or the *borates*.

Of the almost infinite number of compounds belonging to the classes above referred to, only very few need be studied at this stage. It is more important to become acquainted with the general methods of preparation and the general properties of these compounds than to learn details in regard to many individual members of each class. Only those compounds will be considered which well illustrate general principles, or which, owing to some familiar application, happen to be of special interest.

The acids of which the salts are derivatives are already known to us, and in dealing with the acids frequent reference has been made to the methods of making the salts, and to some of their more important properties. It will be well, before taking up the metals systematically, to consider briefly the general methods of preparation and the general properties of the different classes of metallic compounds.

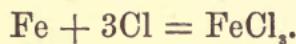
**Chlorides** are made by treating a metal with hydro-

chloric acid or with chlorine ; by treating an oxide or a hydroxide with hydrochloric acid ; by treating a carbonate or any other easily decomposed salt with hydrochloric acid ; by adding hydrochloric acid to a solution containing a metal which with chlorine forms an insoluble compound.

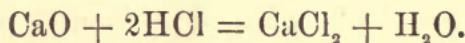
**EXAMPLES.**—Zinc chloride is formed by treating zinc with hydrochloric acid.

[Write the equation.]

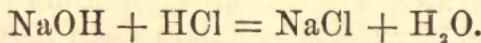
Iron chloride is formed by treating iron with chlorine:



Calcium chloride is formed by treating lime or calcium oxide, CaO, with hydrochloric acid :

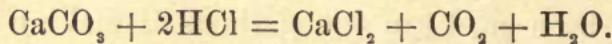


Sodium chloride is formed by treating sodium hydroxide, or caustic soda, NaOH, with hydrochloric acid :



[What takes place when caustic soda or caustic potash is treated with chlorine ?]

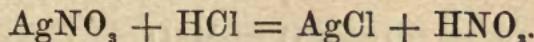
Calcium chloride is formed when calcium carbonate, CaCO<sub>3</sub>, is treated with hydrochloric acid :



Silver chloride is precipitated when hydrochloric acid or a soluble chloride is added to a solution containing a silver salt.

**EXPERIMENT 126.**—Dissolve a small crystal of silver nitrate in pure water. Add to a small quantity of this

solution in a test-tube a few drops of dilute hydrochloric acid. The white substance thus precipitated is silver chloride,  $\text{AgCl}$ . To another small portion of the solution add a few drops of a dilute solution of common salt, or sodium chloride,  $\text{NaCl}$ . The white substance produced in this case is also silver chloride. Add ammonia to each tube. If sufficient be added the precipitates will dissolve. On adding enough hydrochloric acid to these solutions to combine with all the ammonia, the silver chloride is again thrown down. On standing exposed to the light both precipitates change color, becoming finally dark violet. The reactions involved in the above experiments are these: In the first place, when hydrochloric acid is added to silver nitrate this reaction takes place :



When sodium chloride is added this reaction takes place:



In the first reaction nitric acid is set free; in the second, the sodium and silver exchange places. In addition to the insoluble silver chloride, there is formed at the same time the soluble salt, sodium nitrate. On adding ammonia the silver chloride forms with it a compound which is soluble in water; and, on adding an acid, the ammonia combines with it, leaving the silver chloride uncombined and therefore insoluble.

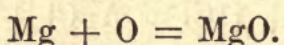
Extensive use is made of insoluble compounds for the purpose of detecting substances in analysis. The principal insoluble chlorides are those of silver, lead, and mercury.\*

\* There are two chlorides of mercury. Only one of them, mercurous chloride, is insoluble.

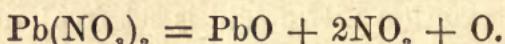
If, therefore, on adding hydrochloric acid or a soluble chloride to a solution, a precipitate is formed, the conclusion is justified that one or more of the three metals—silver, lead, or mercury—is present. By taking account of the differences in the properties of these chlorides it is not difficult to decide of which of them a precipitate consists.

**Oxides.**—These occur very generally in nature, and are among the most common ores of some of the important metals. The oxides of iron, tin, manganese, etc., are all found in nature. They can be made by oxidizing the metals, by heating nitrates and carbonates, and by heating hydroxides.

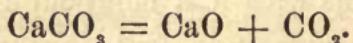
**EXAMPLES.**—When magnesium is burned (see Experiment 14) it is converted into magnesium oxide:



When lead nitrate is heated, it gives off oxygen and an oxide of nitrogen and leaves behind lead oxide:



When calcium carbonate is heated it gives off carbon dioxide and leaves behind calcium oxide, CaO:

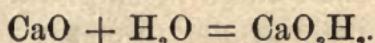


**Hydroxides.**—The hydroxides are formed by treating oxides with water, and by decomposing salts by adding soluble hydroxides.

**EXAMPLES.**—When calcium oxide or lime is treated with water it is converted into the hydroxide,  $\text{CaO}_2\text{H}_2$ , or slaked lime.

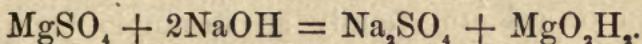
**EXPERIMENT 127.**—To some pieces of freshly slaked lime

add enough cold water to cover it. The action which takes place is represented by the equation



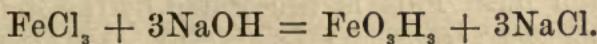
The process is known as slaking. [What evidence have you that heat is evolved in the reaction, and that the substance obtained is not calcium oxide ?]

Most of the hydroxides of the metals are insoluble in water. If a soluble hydroxide is added to a solution containing a metal whose hydroxide is insoluble, the latter is precipitated. Thus, if a solution of sodium hydroxide be added to a solution of a magnesium salt, magnesium hydroxide is precipitated:



**EXPERIMENT 128.**—To a small quantity of a dilute solution of magnesium sulphate add a dilute solution of caustic soda. The white precipitate is magnesium hydroxide. [Would you expect this precipitate to be soluble in sulphuric acid ? in hydrochloric acid ? in nitric acid ?] The answers follow from these considerations: When acids act upon hydroxides, salts are formed; magnesium sulphate is soluble, as is seen by the fact that we started with a solution of this salt; the only insoluble chlorides are those of silver, lead, and mercury; all nitrates are soluble.

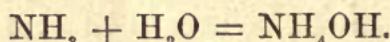
When a solution of an iron salt is treated with sodium hydroxide a precipitate of iron hydroxide is formed:



**EXPERIMENT 129.**—To a dilute solution of that chloride of iron which is known as ferric chloride add caustic soda.

The reddish precipitate which is formed is ferric hydroxide. [From the general statements made above, would you expect this precipitate to be soluble in sulphuric acid? in hydrochloric acid? in nitric acid? Try each.]

Only the hydroxides of the members of the potassium family and of the calcium family are soluble in water. The hydroxides of sodium and potassium are called *alkalies*. The solution of ammonia in water acts like a soluble hydroxide and probably contains ammonium hydroxide,  $\text{NH}_4\text{OH}$ , formed by the action of water on ammonia:



When any one of the soluble hydroxides is added to a salt containing any metal which does not belong to the potassium or calcium family an insoluble compound is thrown down.

[Test this statement by trying such salts as may be available. Note the results in each case. Is an insoluble compound formed? What is its general appearance?]

**Decomposition of Salts by Acids and by Bases.**—The decomposition of salts by the addition of hydroxides is in some respects analogous to the decomposition of salts by the addition of strong acids.

When an acid is added to a salt there are three cases which may present themselves:

1. The acid from which the salt is derived may be volatile or may break up, yielding a volatile product.

In this case decomposition takes place, and the volatile acid is given off. This is illustrated by the liberation of hydrochloric and nitric acids from chlorides and nitrates by the addition of sulphuric acid, and of carbon dioxide from carbonates by the addition of other acids.

[Write the equations representing the action place when sulphuric acid acts upon potassium calcium chloride, sodium nitrate, calcium nitrate hydrochloric acid acts upon sodium carbonate, calcium carbonate.]

2. The acid from which the salt is derived may be insoluble or difficultly soluble in water, and not volatile.

In this case, if the salt is in solution decomposition takes place, and the insoluble or difficultly soluble acid is precipitated. This is illustrated by the liberation of boric acid from borax by the addition of sulphuric acid; and by the liberation of silicic acid by the addition of hydrochloric or sulphuric acid to a soluble silicate.

3. The acid from which the salt is derived may be soluble and not volatile under the existing conditions.

In this case, if the substances are in solution, apparently no change takes place. Thus, when nitric acid is added to sodium chloride in solution no striking change takes place, no gas is given off, no precipitate is formed. It is an extremely difficult thing to determine what does take place under these circumstances. A study of such cases as this is of great importance to chemistry, but cannot be undertaken at this stage.

Now, to return to the action of hydroxides upon salts ; when a soluble base acts upon a salt, three cases may present themselves:

1. The base from which the salt is derived may be volatile or may break up, yielding a volatile product.

In this case decomposition takes place and the volatile base is given off. This is not a common case except among the compounds of carbon. The one illustration which we have had is the decomposition of ammonium salts by calcium hydroxide and sodium hydroxide.

[Write the equations representing the action in both cases. In what does the analogy between the decomposition of ammonium salts by bases and of carbonates by acids consist?]

2. The hydroxide or base from which the salt is derived may be insoluble or difficultly soluble in water, and not volatile.

In this case, if both the salt and the base are in solution, decomposition takes place, and the insoluble or difficultly soluble hydroxide or base is precipitated. This has already been illustrated.

3. The base from which the salt is derived may be soluble and not volatile.

In this case we have no direct evidence of change. Thus, when sodium hydroxide is added to potassium nitrate, nothing is seen except a clear solution. To determine what takes place is a difficult matter.\*

**Sulphides.**—Many sulphides are found in nature. They are made by heating metals with sulphur; by treating solutions of salts with hydrogen sulphide or soluble sulphides.

**EXAMPLES.**—Among the common natural sulphides are iron pyrites,  $\text{FeS}_2$ ; lead sulphide, or galenite,  $\text{PbS}$ ; copper

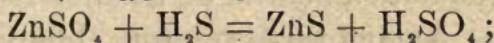
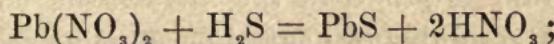
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\* Here a word of warning to students. Do not forget that whenever a precipitate is formed there is something in the solution which is just as important as the precipitate. Accustom yourselves to regard every case of chemical action as a whole. The statement that a precipitate is formed when sodium hydroxide is added to a solution of an iron salt is a very imperfect description of the chemical change that takes place. Precipitates have come to be regarded in a false light, in consequence of the constant use made of them for purposes of analysis. *It must be remembered that analysis is not chemistry*, though it is essential to the study of chemistry and is an important application of the science. The art of analysis is founded upon a knowledge of the science of chemistry. If you have a knowledge of the science, it will be easy to acquire the art of analysis, should this acquisition become desirable.

pyrites,  $\text{FeCuS}_2$ . [Examine several specimens of each, and note their general properties.]

When copper or iron is heated with sulphur the corresponding sulphides are formed. (See Experiments 10 and 112.) [For what purpose were these experiments performed?]

When hydrogen sulphide is passed through a solution containing a metal whose sulphide is insoluble, the sulphide is precipitated. This has been illustrated by passing the gas through solutions of lead nitrate, zinc sulphate, and arsenic trioxide. The reactions are :



[What differences were observed in these three cases? Repeat the experiments.]

When a soluble sulphide, as ammonium sulphide or sodium sulphide, is added to a solution containing a metal whose sulphide is insoluble, the insoluble sulphide is thrown down. Add ammonium sulphide successively to dilute solutions of an iron salt, a lead salt, a copper salt. Note what takes place in each case.

The sulphides of all the metals except those which belong to the lithium and calcium families, and that of magnesium, are insoluble in water. Of those sulphides which are insoluble in water, some are insoluble and some are soluble in dilute hydrochloric acid. Further, of those which are insoluble in dilute hydrochloric acid, some are soluble and some are insoluble in ammonium sulphide.

These facts furnish the basis of the method most commonly made use of in analyzing substances. Suppose we have a

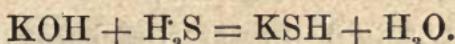
solution containing all the more common elements, and we wish to determine what is in it. [If, on adding hydrochloric acid, a precipitate is formed, what does this show?] This precipitate is filtered off, and treated with hydrogen sulphide. Those metals whose sulphides are insoluble in dilute hydrochloric acid will be precipitated. Among the elements which may be contained in this precipitate are lead, mercury, copper, tin, arsenic. The solution from which the precipitate was thrown down may still contain those metals whose sulphides are soluble in dilute hydrochloric acid. If, therefore, we filter off the precipitate and add ammonium sulphide to the filtrate, the metals whose sulphides are insoluble in neutral or alkaline solutions will be thrown down. Among these are iron, aluminium, chromium, manganese, etc. The filtrate from this precipitate may contain all those metals whose sulphides are soluble in water. By means of other reactions these can be subdivided into groups. In the ordinary method of analysis we have, therefore, several groups of elements to deal with. These are :

1. *The hydrochloric-acid group*, consisting of those metals whose chlorides are insoluble in water.
2. *The hydrogen-sulphide group*, consisting of those metals whose sulphides are insoluble in dilute hydrochloric acid.
3. *The ammonium-sulphide group*, consisting of those metals whose sulphides are soluble in dilute hydrochloric acid, but are precipitated by ammonium sulphide.
4. Elements whose sulphides are soluble in water.

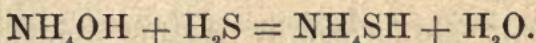
Each of these groups can be subdivided, and the sub-groups again subdivided, until positive evidence of the presence of certain metals is obtained.

*Hydrosulphides* are formed when hydrogen sulphide is passed into a solution of a hydroxide until no more is taken up.

Potassium hydrosulphide is formed thus:



Ammonium hydrosulphide is formed thus:



**Nitrates.**—These salts are formed by treating metals with nitric acid; by treating oxides or hydroxides with nitric acid, and in general by treating any easily decomposed salt as a carbonate with nitric acid.

**EXAMPLES.**—When nitric acid acts upon copper, copper nitrate is formed. [What else is formed? Give an account of the changes which take place. Write the equation representing the reaction.]

The simple neutralization of nitric acid with a base or hydroxide has been illustrated in the experiments on acids and bases (Experiment 61). [Write the equations representing the reactions which take place when nitric acid is neutralized with potassium hydroxide, with calcium oxide, with calcium hydroxide.]

All nitrates are soluble in water, and all are decomposed by heat. [Try the solubility, in water, of such nitrates as may be available.]

**EXPERIMENT 130.**—Heat 2 to 3 grams potassium nitrate on charcoal with the blow-pipe flame. The decomposition with evolution of gas is called *deflagration*. Heat some copper nitrate and lead nitrate. Carefully note the changes

which take place. The compounds left behind are copper oxide and lead oxide.

**Chlorates** are made from potassium chlorate, which is made by treating a strong solution of caustic potash with chlorine. [Explain the reaction.]

Chlorates are soluble in water, and are decomposed by heat with evolution of oxygen. [When potassium chlorate is heated, what takes place in the first stage of the operation?]

*Hypochlorites* are formed by treating some of the metallic hydroxides in dilute solution with chlorine. This has been illustrated in the formation of "bleaching-powder," which contains calcium hypochlorite. [Explain what takes place when slaked lime is treated with chlorine.]

Hypochlorites are decomposed by heat.

**Sulphates.**—Some sulphates, as those of calcium and barium, are found in nature, the former being known as *gypsum*. Sulphates are made by treating metals or metallic hydroxides or oxides with sulphuric acid; by treating easily decomposed salts, as carbonates, with sulphuric acid; and by treating a solution containing a metal whose sulphate is insoluble with sulphuric acid or a soluble sulphate.

**EXAMPLES.**—Usually, when sulphuric acid acts upon a metal, hydrogen is evolved and a salt is formed. This has been illustrated in the preparation of hydrogen by means of zinc and sulphuric acid.

**EXPERIMENT 131.**—Dissolve some iron in dilute sulphuric acid. When the acid is neutralized, filter the solution and evaporate it down to crystallization. [What is the appearance of the salt? Does it contain water of crystallization? Was hydrogen evolved during the action of the

acid on the metal?] Dry some of the salt, and put it aside for further use.

**EXPERIMENT 132.**—Dissolve some copper foil in concentrated sulphuric acid. [In what respect does the action in this case differ from that in the last experiment?] Evaporate the solution, and get out some of the salt in the form of crystals. [What is the appearance of the salt? Does it contain water of crystallization? What does the salt look like after it has been heated in a tube?] Dry some of it, and put it aside for further use. [Write the equations representing the action which takes place when copper acts upon sulphuric acid.]

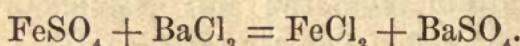
The action of sulphuric acid on metallic hydroxides has been illustrated. (See Experiment 61.)

[Write the equation representing the action which takes place when the acid acts upon sodium hydroxide, potassium hydroxide, ammonium hydroxide. What is monosodium sulphate? What is neutral sodium sulphate? Is there any difference between disodium sulphate and neutral sodium sulphate?]

Most sulphates are soluble in water. The sulphates of barium, strontium, and lead are insoluble in water, and the sulphate of calcium is difficultly soluble. Therefore, if sulphuric acid be added to a solution containing either of the metals barium, strontium, or lead, a precipitate will be formed.

**EXPERIMENT 133.**—Make a dilute solution of barium chloride, of lead nitrate, of strontium nitrate. To a small quantity of each in a test-tube add a little sulphuric acid. In each case a white precipitate is formed. [What remains in solution?] Make a somewhat concentrated solution of calcium chloride. To this add some sulphuric acid. A

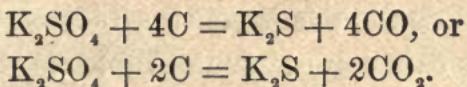
precipitate is formed. [What is in solution?] Add more water, and see whether this precipitate will dissolve. The formulas of the salts used in the experiments are barium chloride,  $\text{BaCl}_2$ ; lead nitrate,  $\text{Pb}(\text{NO}_3)_2$ ; strontium nitrate,  $\text{Sr}(\text{NO}_3)_2$ . [Write the equations expressing the reactions.] If to the solutions of the salts any soluble sulphate be added instead of sulphuric acid, the same insoluble sulphates will be formed. The sulphates of iron, copper, sodium, and potassium are among the soluble sulphates. Make dilute solutions of small quantities of each of these, and add them successively to the solutions of barium chloride, lead nitrate, and strontium nitrate. The formula of iron sulphate is  $\text{FeSO}_4$ ; of copper sulphate,  $\text{CuSO}_4$ ; of sodium sulphate,  $\text{Na}_2\text{SO}_4$ ; and of potassium sulphate,  $\text{K}_2\text{SO}_4$ . Write the equations representing the reactions which take place in the above experiments. It need hardly be explained that the action consists in an exchange of places on the part of the metals. Thus, when the soluble salt iron sulphate,  $\text{FeSO}_4$ , is brought together with the soluble salt barium chloride,  $\text{BaCl}_2$ , the insoluble salt barium sulphate,  $\text{BaSO}_4$ , and the soluble salt iron chloride,  $\text{FeCl}_2$ , are formed:



As a rule, sulphates are not decomposed by heat.

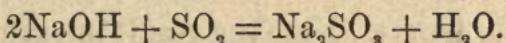
**EXPERIMENT 134.**—Heat successively specimens of the sulphates of sodium, potassium, iron, and copper in a porcelain crucible over the flame of a Bunsen burner or an alcohol lamp. After cooling, see whether the substances left in the crucible are sulphates. Dissolve in water and add to a solution of barium chloride.

When heated with charcoal in the reducing flame of the blow-pipe, sulphates are reduced to sulphides:

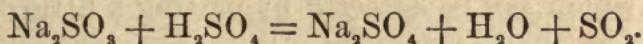


**EXPERIMENT 135.**—Mix and moisten a little sodium sulphate and finely powdered charcoal. Heat the mixture for some time in the reducing flame. After cooling scrape off the salt, dissolve it in a few cubic centimetres of water and filter through a small filter. If the change to the sulphide has taken place, sodium sulphide,  $\text{Na}_2\text{S}$ , is in solution. A soluble sulphide when added to a solution containing copper gives a black precipitate of copper sulphide. Try this; also try the action on copper of some of the sulphate from which the sulphide was made.

**Sulphites** are made from sodium or potassium sulphite, which are made by treating sodium or potassium hydroxide in solution with sulphur dioxide:



All sulphites are decomposed by the common acids, sulphur dioxide being given off:



**Carbonates.**—Many carbonates are found in nature, some of them in great abundance, and widely distributed. The principal one is calcium carbonate. They are made by passing carbon dioxide into solutions of hydroxides, and by adding soluble carbonates to solutions of salts containing metals whose carbonates are insoluble.

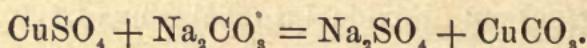
**EXAMPLES.**—The formation of potassium carbonate by the treatment of potassium hydroxide with carbon dioxide has already been illustrated. (See Experiments 93 and 94.)

[Write the equation representing the action. Is the salt formed in this case soluble or insoluble in water ?]

The formation of calcium carbonate by passing carbon dioxide into a solution of calcium hydroxide (lime-water) has been illustrated under the head of carbon dioxide.

[Describe the experiment. Write the equation representing the action in this case. Is calcium carbonate soluble or insoluble in water ? In hydrochloric acid, in sulphuric acid, in nitric acid ? What action takes place with each of these acids ?]

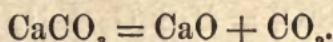
**EXPERIMENT 136.**—The formation of carbonates by the addition of soluble carbonates to solutions of salts of metals whose carbonates are insoluble is illustrated by the following experiments : Make solutions of copper sulphate, iron sulphate, lead nitrate, silver nitrate, calcium chloride, barium chloride. Add to each a little of a solution of a soluble carbonate, as sodium carbonate, potassium carbonate, ammonium carbonate. Note the result in each case. Filter off all the precipitates and prove that they are carbonates. This may be done by treating them with dilute acids, which decompose them, causing an evolution of carbon dioxide, which can be detected by passing a little of it into lime-water. Write all the equations representing the reactions which take place in the above experiments. Here again, as in the experiments with the sulphates, the metals exchange places :



[Is copper bivalent or univalent if the formula of copper sulphate is  $\text{CuSO}_4$ ?]

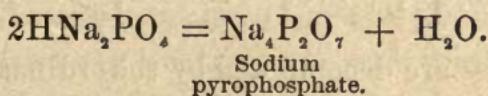
All carbonates except those of the members of the potassium family are insoluble, and are decomposed by heat into

carbon dioxide and the oxide of the metal. The decomposition of calcium carbonate into lime and carbonate is the best-known illustration of this fact :

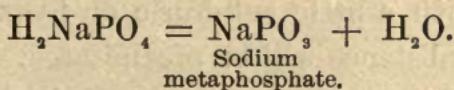


**Phosphates.**—Calcium phosphate is very abundant in nature, and a few other phosphates are also found. The methods for making phosphates are in principle the same as those used for making sulphates.

The phosphates of all the metals except the members of the potassium family are insoluble in water. The normal phosphates [what is a normal phosphate ?], as a rule, are not changed by heat. Those phosphates in which two thirds of the hydrogen is replaced by metal—as, for example, disodium phosphate,  $\text{HNa}_2\text{PO}_4$ —lose water when heated, and yield pyrophosphates :



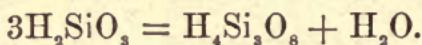
Those phosphates in which only one third of the hydrogen is replaced by metal—as, for example, monosodium phosphate,  $\text{H}_2\text{NaPO}_4$ —lose water when heated, and yield metaphosphates :



Neither the pyrophosphates nor metaphosphates are changed by heat.

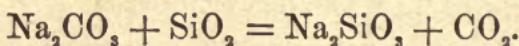
**Silicates.**—The extensive occurrence of silicates in nature has been spoken of. Those which are most abundant are the *feldspars* and their decomposition products. The prin-

cipal feldspar is a complex silicate of aluminium and potassium, of the formula  $KAlSi_3O_8$ , derived from the polysilicic acid  $H_4Si_3O_8$  [what is a polysilicic acid ?]:



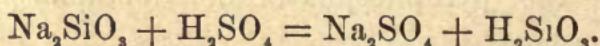
Silicates may be made by heating together at a high temperature silicon dioxide, in the form of fine sand, and bases.

**EXPERIMENT 137.**—Mix together some fine sand and about four times its weight of a mixture of potassium and sodium carbonates. Heat in a platinum crucible in the flame of the blast-lamp\* until the mass is thoroughly melted. Pour the molten mass out on a stone, and when cooled break it up and treat it with water. What passes into solution is a mixture of potassium and sodium silicates:



Some silicates are decomposed by the ordinary acids, such as sulphuric and nitric acids, the silicic acid separating as a difficultly soluble substance, which loses water and becomes insoluble.

**EXPERIMENT 135.**—Treat a little of the solution containing sodium and potassium silicates, prepared in the last experiment, with a little sulphuric or hydrochloric acid. A gelatinous substance will be precipitated. This is silicic acid. Some of the acid remains in solution:



By evaporating the solution to dryness and heating for

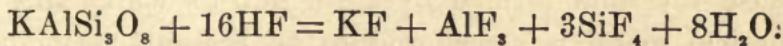
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\* This is nothing but a large blow-pipe worked by a foot-bellows.

a time on the water-bath, all the silicic acid is converted into silicon dioxide, which is entirely insoluble.

Many silicates which are not acted upon by strong acids are decomposed by fusing with sodium or potassium carbonate.

Silicates which are not decomposed in either of the ways mentioned yield to hydrofluoric acid. The action consists in the formation of the gas, silicon tetrafluoride,  $\text{SiF}_4$ , and the fluorides of the metals present. Thus, the reaction in the case of feldspar takes place in accordance with the equation



The silicon fluoride is given off and the fluorides of the metals are soluble in water. Hence hydrofluoric acid *dissolves* the silicate. [Is this use of the word *dissolves* strictly correct?]

Having thus briefly considered some of the chief methods of preparation and the principal general properties of the compounds of the metals, we may now take up such facts in regard to the individual metals and their derivatives as are of special interest. It must be borne in mind that a thorough knowledge of the chemistry of these substances can only be acquired by a long course of laboratory practice.

## CHAPTER XVIII.

### THE POTASSIUM FAMILY: LITHIUM, SODIUM, POTASSIUM, CÆSIUM, RUBIDIUM (AMMONIUM).

THE most widely distributed and hence best-known members of this family are sodium and potassium. The hypothetical metal ammonium is included in the family because the salts formed by ammonia, in which this hypothetical metal is considered to be present, very closely resemble the salts of potassium and sodium. The members of the family are generally called the *metals of the alkalies*, as the two best-known members are obtained from the alkalies, caustic potash and caustic soda, or potassium and sodium hydroxides.

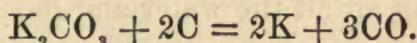
**Potassium, K (At. Wt. 39).**—This element is a constituent of many minerals, particularly of feldspar, which, as already explained, is a complex silicate of aluminium and potassium. The natural decomposition of minerals containing potassium gives rise to the presence of this metal, in various forms of combination everywhere in the soil. It is taken up by plants; and when vegetable material is burned the potassium remains behind, chiefly as potassium carbonate. When wood-ash is treated with water the potassium carbonate is dissolved, and it may be obtained in an impure state by evaporating the solution. The substance thus obtained is called *potash*.

**EXPERIMENT 139.**—Treat two or three litres of wood-ashes with water. Filter off the solution, and examine it

by means of red litmus-paper. The color of the paper is changed to blue. Plainly the solution is alkaline. Examine some potassium carbonate. [Does its solution act in the same way?] Evaporate the solution to dryness. Collect the dry residue and treat it with dilute hydrochloric acid. [Is a gas given off? Is it carbon dioxide?]

Potassium is also found in the form of the chloride KCl, accompanying the chloride of sodium, and as the nitrate in saltpetre.

The metal was first prepared by the action of a powerful electric current on potassium hydroxide. It is now manufactured by distilling a mixture of potassium carbonate and charcoal:



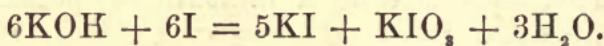
It is a light substance, which floats on water. [Have you had evidence of this?] Its freshly cut surface has a bright metallic lustre, almost white; it acts upon water with great energy, causing the evolution of hydrogen, which burns, and the formation of potassium hydroxide. This reaction has already been considered in connection with hydrogen. [Turn back to the experiment (Experiment 27) and perform it again. It will now appear much clearer.] In consequence of its action on water, potassium cannot be kept in the air. It is kept under some oil upon which it does not act, as petroleum.

**Compounds of Potassium.**—The chief compounds of potassium with which we meet are the *iodide*, KI, which is extensively used in medicine and in photography; the *hydroxide*, or caustic potash, KOH, which finds extensive use in laboratories; the *nitrate*, or saltpetre, KNO<sub>3</sub>, used in the manufacture of gunpowder; the *chlorate*, KClO<sub>3</sub>,

used in the preparation of oxygen and in medicine; and the *carbonate*,  $K_2CO_3$ .

The methods used in preparing some of these compounds are interesting, as illustrating the applications of the principles of chemistry.

**Potassium iodide,  $KI$ ,** is made by treating caustic potash with iodine until the solution begins to show a permanent yellow color, which is an indication that no more iodine will be taken up. The action is the same as that which takes place when chlorine acts upon warm concentrated caustic potash. Both the iodide and iodate are formed :



By evaporating off all the water and heating the residue, the iodate is decomposed into iodide and oxygen.

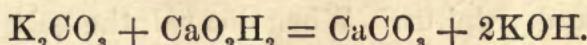
**EXPERIMENT 140.**—Examine a bottle of crystallized potassium iodide. Taste a little. Dissolve some in water. Add some iodine to this solution. [Does the iodine dissolve?] Heat a little. [Does it contain water of crystallization?] Treat a crystal or two with a few drops of concentrated sulphuric acid. [What takes place? To what is the appearance of violet vapors due? How many gases are given off? (See Experiment 107.)]

**Potassium Hydroxide,  $KOH$ .**—This well-known substance, commonly called caustic potash, is prepared by treating potassium carbonate with calcium hydroxide in a silver or iron vessel.

**EXPERIMENT 141.**—Dissolve 50 grams potassium carbonate in 500 to 600 cc. water. Heat to boiling in an iron or silver vessel, and gradually add the slaked lime obtained from 25 to 30 grams of good quick-lime. During the operation the mass should be stirred with an iron spatula.

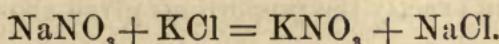
After the solution is cool, draw it off by means of a siphon into a bottle. This may be used in experiments in which caustic potash is required.

The reaction is based upon the fact that calcium carbonate is insoluble, and that potassium carbonate and calcium hydroxide are soluble:



The hydroxide is a white brittle substance. In contact with the air it deliquesces [what does this mean?] and absorbs carbon dioxide. It is a very strong base. [Explain the action which takes place when potassium hydroxide acts upon ammonium chloride,  $\text{NH}_4\text{Cl}$ ; copper sulphate,  $\text{CuSO}_4$ ; and magnesium nitrate,  $\text{Mg}(\text{NO}_3)_2$ .]

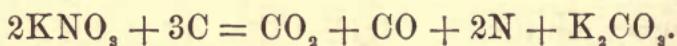
**Potassium Nitrate,  $\text{KNO}_3$ .**—This salt is commonly called *saltpetre*. Its occurrence in nature has already been spoken of under Nitric Acid. [What are the conditions which give rise to its formation?] When refuse animal matter is left to undergo decomposition in the presence of bases, nitrates are always the end-products. Advantage is taken of this fact for the purpose of preparing saltpetre artificially, the process being carried on on the large scale in the “saltpetre plantations.” Most of the saltpetre which is in the market is made from Chili saltpetre, or sodium nitrate, by treating it with potassium chloride:



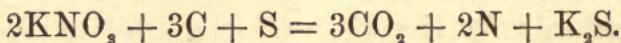
Potassium nitrate crystallizes in long rhombic prisms of salty taste.

It is used in the preparation of sulphuric acid [what rôle does it play in the preparation of sulphuric acid?], and of nitric acid [how is nitric acid obtained from it?]. Its chief

use is in the manufacture of gunpowder. The value of gunpowder is due to the fact that it *explodes* readily, the explosion being a chemical change accompanied by a sudden evolution of gases. When the powder is enclosed in a gun-barrel the gases in escaping drive the ball before them. Gunpowder is made of a mixture of saltpetre, charcoal, and sulphur. When heated the saltpetre gives off oxygen and nitrogen; the oxygen combines with the charcoal, forming carbon dioxide and carbon monoxide, and the sulphur combines with the potassium, forming potassium sulphide. When a mixture of saltpetre and charcoal is burned, the reaction which takes place is this :



By adding the necessary quantity of sulphur the carbon dioxide, which would otherwise remain in combination with the potassium as potassium carbonate, is given off and potassium sulphide formed :



**EXPERIMENT 142.**—Mix together 15 grams potassium nitrate and 2.5 grams powdered charcoal. Set fire to the mass.

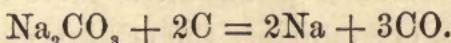
[**PROBLEM.**—What would be the volume at 760 mm. and 0° of the gases evolved from 5 grams of gunpowder containing the constituents in exactly the proportions given above?]

**Potassium Chlorate,  $\text{KClO}_3$ .**—This salt has so frequently been referred to and used in earlier experiments that it is not necessary to say anything more about it here.

[Describe the method of preparation and decomposition by heat. What takes place when it is treated with sulphuric acid?]

**Sodium, Na (At. Wt. 23).**—Sodium occurs very widely distributed and in large quantities, principally as sodium chloride. It occurs also as sodium nitrate, and in the form of silicate in many minerals. It is found everywhere in the soil, and is taken up by plants, especially by those which grow in the neighborhood of the sea-shore and in the sea.

It is prepared from sodium carbonate by the same method as that used in the preparation of potassium, the reaction involved being represented thus :



Its properties are very similar to those of potassium. It is light, floating on water; it has a bright metallic lustre, and is soft. It decomposes water, but not as actively as potassium.

[Describe what takes place when a small piece of potassium is thrown upon water and when a piece of sodium is similarly treated. How is the difference accounted for?]

Sodium has a strong affinity for oxygen, and is used in some chemical processes as a reducing agent [what is a reducing agent?], as, for example, in the preparation of silicon, magnesium, and aluminium. A compound of mercury and sodium, known as sodium amalgam, is used in some metallurgical operations connected with the extraction of silver and gold from their ores.

The chief compounds of sodium are the *chloride*,  $\text{NaCl}$ ; the *hydroxide*, or caustic soda,  $\text{NaOH}$ ; the *nitrate*, or Chili saltpetre,  $\text{NaNO}_3$ ; the *sulphate*,  $\text{Na}_2\text{SO}_4$ ; the *carbonate*,  $\text{Na}_2\text{CO}_3$ ; and the *borate*, or borax,  $\text{Na}_2\text{B}_4\text{O}_7$ .

**Sodium Chloride,  $\text{NaCl}$ .**—This is the substance which is known by the name *common salt*. It occurs very widely

distributed, and, as it is easily soluble, much of the water which enters into the ocean contains some of it in solution. Sea-water contains from  $2\frac{1}{2}$  to 3 per cent. In some places the salt is taken out of mines in solid form; in others, water is allowed to flow into the mines, and to remain for some time in contact with the salt, and the solution thus formed is drawn or pumped out of the mine, and evaporated by appropriate methods.

Sodium chloride crystallizes in colorless and transparent cubes. Sometimes that which occurs in nature is colored blue. In hot water it is but little more soluble than in cold water. In crystallizing, the crystals enclose water not as water of crystallization, and this is given off when the crystals are heated, the action being accompanied by a crackling sound.

Salt is used as the starting-point in the preparation of all sodium compounds and of chlorine and hydrochloric acid.

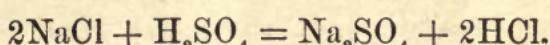
[How are chlorine and hydrochloric acid obtained from it? What takes place when a solution of silver nitrate is added to a solution of common salt? What substances besides silver nitrate act in the same way?]

**Sodium Hydroxide, NaOH.**—This is commonly called caustic soda. It can be prepared in the same way as potassium hydroxide; that is, by treating a solution of sodium carbonate with lime. [Explain the reaction.] Its properties are very similar to those of caustic potash [Are the hydroxides of the metals mostly soluble or insoluble substances?]

**Sodium Nitrate, NaNO<sub>3</sub>.**—This is the salt which has so frequently been referred to by the name Chili saltpetre. It occurs in very large quantities, and is the chief source of nitric acid. It is cheaper than potassium nitrate, but can-

not be substituted for it in the manufacture of gunpowder, because it becomes moist in the air.

**Sodium Sulphate,  $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ .**—The common name of this substance is Glauber's salt. It is manufactured in enormous quantities for the purpose of converting common salt into sodium carbonate, or "soda":

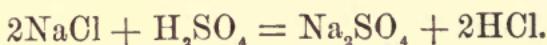


[What becomes of the hydrochloric acid which is given off?]

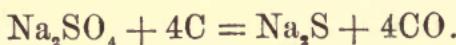
The salt crystallizes in large colorless monoclinic prisms, containing 10 molecules of water of crystallization,  $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ . It loses water when left in contact with the air. [Is it efflorescent or deliquescent?]

**Sodium Carbonate,  $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$ .**—This salt, commonly called *soda*, is one of the most important of manufactured chemical substances. The mere mention of the fact that it is essential to the manufacture of glass and soap will serve to give some conception of its importance. It is found in the ashes of sea plants, just as potassium carbonate is found in the ashes of those plants which grow on the land. We are, however, not dependent on sea plants for our supply, as two methods have been devised for preparing sodium carbonate from sodium chloride, with which nature provides us in such abundance. As these methods are interesting applications of chemical principles, it will be well to consider them briefly. The problem to be solved is to convert sodium chloride,  $\text{NaCl}$ , into sodium carbonate,  $\text{Na}_2\text{CO}_3$ . The process devised by Le Blanc for the French government during the Revolution, when the supply had been cut off, involves four reactions:

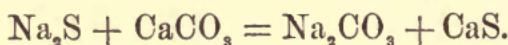
1st. The sodium chloride is converted into sodium sulphate by treating it with sulphuric acid:



2d. The sodium sulphate thus obtained is heated with charcoal, which reduces it to sodium sulphide,  $\text{Na}_2\text{S}$ :

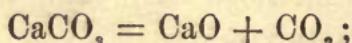


3d. The sodium sulphide is heated with calcium carbonate, when sodium carbonate and calcium sulphide are formed:



4th. But both the products of this reaction are soluble in water. If lime is present it forms, however, an insoluble compound with calcium sulphide,  $3\text{CaS}\cdot\text{CaO}$ , and this can easily be separated from the sodium carbonate.

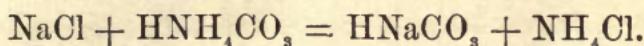
In practice the sodium sulphate is mixed with charcoal and calcium carbonate, and the mixture heated. The charcoal reduces the sulphate to the sulphide, which acts upon the calcium carbonate, forming sodium carbonate and calcium sulphide. But some of the calcium carbonate is decomposed by the heat into lime and carbon dioxide:



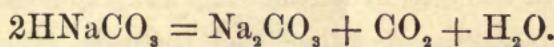
and the lime thus formed combines with calcium sulphide to form the above-mentioned insoluble compound. On treating the mass with water after cooling, sodium carbonate is dissolved.

Another process which is now extensively used is the so-called *ammonia-soda process*. This depends upon the fact that monosodium carbonate,  $\text{HNaCO}_3$ , is comparatively

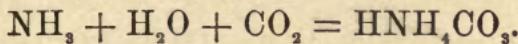
difficultly soluble in water. If, therefore, monoammonium carbonate, or acid ammonium carbonate,  $\text{HNH}_4\text{CO}_3$ , is added to a solution of common salt, acid sodium carbonate,  $\text{HNaCO}_3$ , crystallizes out, and ammonium chloride remains behind in the solution:



When the acid carbonate is heated, it gives off carbon dioxide, and is converted into the normal salt thus:



The carbon dioxide given off is passed into ammonia, and thus again obtained in the form of acid ammonium carbonate:



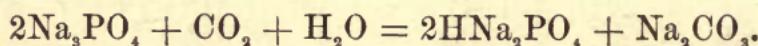
The ammonium chloride obtained in the first reaction is treated with lime or magnesia,  $\text{MgO}$ , and the ammonia set free. This ammonia is again used in the preparation of acid ammonium carbonate.

**EXPERIMENT 143.**—Pass carbon dioxide into a strong solution of ammonia (about 100 cc.) until it is no longer absorbed. A solution of acid ammonium carbonate is thus obtained. Add this to a strong solution of sodium chloride as long as a precipitate is formed. Filter off the precipitate, and dry it by spreading it upon layers of filter paper. Heat some of the salt when dry, and determine whether the gas given off is carbon dioxide or not. When gas is no longer given off by heat, let the tube cool and examine the residue. [Is it a carbonate?]

Sodium carbonate crystallizes in large monoclinic prisms

with 10 molecules of water of crystallization. The crystals are efflorescent.

**Disodium Phosphate,  $\text{HNa}_2\text{PO}_4 + 12\text{H}_2\text{O}$ .**—This is the common form of sodium phosphate. It is formed when phosphoric acid is treated with sodium carbonate until the solution begins to show an alkaline reaction with red litmus. It is a remarkable fact that, although phosphoric acid is tribasic, and with most metals forms salts which are derived from the acid by replacement of all the three hydrogen atoms, as  $\text{Ag}_3\text{PO}_4$ ,  $\text{Ca}_3(\text{PO}_4)_2$ , etc., with sodium its most stable salt is the one in which two hydrogen atoms are replaced by sodium. A salt of the formula  $\text{Na}_3\text{PO}_4$  can be made, but it has an alkaline reaction, and absorbs carbon dioxide from the air, being converted into sodium carbonate and disodium phosphate:



**Sodium Borate,  $\text{Na}_2\text{B}_4\text{O}_7 + 10\text{H}_2\text{O}$ .**—This salt has been referred to under boric acid. It is commonly called *borax*. It is found in nature in several lakes in Asia, and in this country in Clear Lake, Nevada. It is manufactured by neutralizing the boric acid found in Tuscany.

When heated, borax puffs up, and at red heat melts, forming a transparent colorless liquid. This is anhydrous borax,  $\text{Na}_2\text{B}_4\text{O}_7$ . Molten borax has the power to dissolve metallic oxides, and forms colored glasses with some of them. It is used in blow-pipe work (see Boric Acid). Borax is an antiseptic; that is to say, it prevents the decomposition of organic substances.

**Ammonium Salts.**—The method of formation of the so-called ammonium salts has been described (see Ammonia).

So here May 6<sup>th</sup>

These salts resemble the salts of potassium and sodium in many respects, and they are hence described in the same connection. The chief ones are the *chloride*,  $\text{NH}_4\text{Cl}$ ; the *carbonate*,  $(\text{NH}_4)_2\text{CO}_3$ ; the *sulphide*,  $(\text{NH}_4)_2\text{S}$ ; and the *hydrosulphide*,  $(\text{NH}_4)\text{HS}$ .

**Ammonium Chloride,  $\text{NH}_4\text{Cl}$ .**—This salt is commonly called *sal-ammoniac*. At present its principal source is the gas-works. The ammoniacal liquor of the works is neutralized with hydrochloric acid, and the salt obtained by evaporation. It has a sharp, salt taste, and is easily soluble in water. When heated it is converted into vapor without melting, and with very slight decomposition; and when the vapor comes in contact with a cold surface, it condenses in the form of crystals. This process of vaporizing and condensing a solid is called *sublimation*.

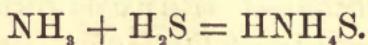
**EXPERIMENT 144.**—On a piece of platinum foil or porcelain heat a little pure ammonium chloride. It will pass off and form a dense white cloud. This is the same cloud as that formed by bringing together gaseous ammonia and hydrochloric acid. *All ammonium salts are either volatile or decompose when heated.*

[What takes place when ammonium chloride is treated with caustic soda? with lime? with sulphuric acid?] 2

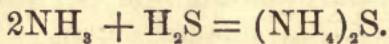
**Ammonium Sulphide,  $(\text{NH}_4)_2\text{S}$ .**—This substance is extensively used in chemical analysis for the purpose of precipitating those sulphides which are soluble in dilute hydrochloric acid. As will be remembered, in analyzing a mixture of substances the first thing usually done is to add hydrochloric acid to the solution. This precipitates silver, lead, and, under certain conditions, mercury. This precipitate having been filtered off, hydrogen sulphide is passed through the filtrate, when those metals whose sulphides are

insoluble in dilute hydrochloric acid are thrown down. The precipitate is filtered off and ammonium sulphide added to the filtrate, when the metals whose sulphides are soluble in dilute hydrochloric acid are thrown down. Among these are iron, cobalt, nickel, manganese, etc. Any other soluble sulphide might be used, but the advantage of ammonium sulphide is that it is volatile, and, hence, by evaporating the solution and heating, it can be gotten rid of.

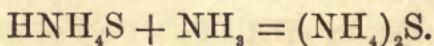
Ammonium sulphide is made by passing hydrogen sulphide into an aqueous solution of ammonia. If the gas is passed until the solution is saturated, the product is the hydrosulphide  $\text{HNH}_4\text{S}$ :



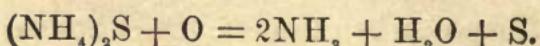
If only half this quantity of the gas is passed, the product is the sulphide:



The simplest way to make it is to divide a quantity of ammonia solution into two equal parts. Saturate one half, thus forming the hydrosulphide, and add the other half, when this reaction takes place:



The product is a colorless liquid of a disagreeable odor. It soon changes color, becoming yellow, and after a time a yellow deposit is formed in the vessel in which it is contained. This change of color is due to the action of the oxygen of the air. Some of the sulphide is decomposed into ammonia, water, and sulphur:



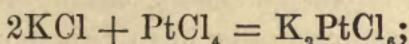
The sulphur thus set free combines with the undecomposed ammonium sulphide, forming the compounds  $(\text{NH}_4)_2\text{S}_2$ ,  $(\text{NH}_4)_2\text{S}_3$ , etc., known as *polysulphides*. When as much sulphur as possible has been taken up in this way, any more which may be set free by the action of oxygen is deposited.

A solution containing the polysulphides is called *yellow ammonium sulphide*. It is used to dissolve the sulphides of arsenic, antimony, and tin in analytical operations. (See description of method of analysis, p. 296.)

**EXPERIMENT 145.**—Saturate 100 cc. strong aqueous ammonia with hydrogen sulphide. Add to the saturated solution 100 cc. of the same ammonia.

**Ammonium Hydrosulphide,  $\text{HNH}_4\text{S}$ .**—As stated above, a solution of this substance is made by passing hydrogen sulphide into a solution of ammonia until no more is taken up.

**General Characteristics of the Metals of the Alkalies.**—From what has been said, it will be seen that nearly all the compounds of these metals are soluble in water. Of those mentioned only monosodium carbonate is at all difficultly soluble. There are a few insoluble salts of potassium, those which are chiefly used in analytical operations being the *chloro-platinate*,  $\text{K}_2\text{PtCl}_6$ , which is formed by adding a solution of platinum chloride,  $\text{PtCl}_4$ , to a solution containing potassium chloride:



and the *fluo-silicate*,  $\text{K}_2\text{SiF}_6$ , which is formed when a solution of hydrofluo-silicic acid,  $\text{H}_2\text{SiF}_6$ , is added to a solution containing potassium.

**EXPERIMENT 146.**—Add platinum chloride and hydro-

fluosilicic acid successively to solutions containing potassium chloride.

The elements *lithium*, *cæsium*, and *rubidium* are much rarer than sodium and potassium. While for the chemist their study is of importance, for the beginner it is not necessary. Lithium is found in a form of *mica* known as *lepidolite*. It is the lightest metal known, and has the smallest atomic weight, viz., 7. The relations between the atomic weights of the members of this family are similar to those already noticed between chlorine, bromine, and iodine; sulphur, selenium, and tellurium; and phosphorus, arsenic, and antimony. Thus, we have lithium, 7; sodium, 23; and potassium, 39. The atomic weight of sodium, 23, is the mean of those of lithium, 7, and potassium, 39.

$$\frac{7 + 39}{2} = 23.$$

Similarly, the atomic weight of rubidium, 85, is nearly the mean of those of potassium and cæsium, 133:

$$\frac{39 + 133}{2} = 86.$$

**Flame Reactions and the Spectroscope.**—When a clean piece of platinum wire is held for some time in the flame of the Bunsen burner, it then imparts no color to the flame. If now a small piece of sodium carbonate or any other salt of sodium be put on it, the flame is colored intensely yellow. All sodium compounds have this power, and hence the chemist makes use of the fact for the purpose of detecting the presence of sodium. Similarly, potassium compounds color the flame violet; lithium compounds color the flame red; and the other metals of the family also impart characteristic colors to the flame.

**EXPERIMENT 147.**—Prepare some pieces of platinum wire, 8 to 10 c.m. long, with a loop on the end like those described for blow-pipe work. After thoroughly cleaning them, insert one in a little sodium carbonate, and notice the color it gives to the flame. Try another with potassium carbonate, and, if the substances are available, others with a lithium compound, a cæsium, and a rubidium compound.

While it is an easy matter to recognize potassium alone, or any one of the other metals alone, it is difficult to do so when they are together in the same compound. For example, when potassium and sodium are together, the intense yellow caused by the sodium completely masks the more delicate violet caused by the potassium, so that the latter cannot be seen with the unaided eye. In this particular case we can get over the difficulty by letting the light pass through a blue glass, or a thin glass vessel filled with a solution of indigo. The yellow light is thus cut off while the violet light passes through and can be recognized. A more general method for detecting the constituents of light is by means of a prism. Lights of different colors are turned out of their course to different extents when passed through a prism, as is seen when white sunlight is passed through a prism. A narrow beam of white light passing in emerges as a band of various colors, called its *spectrum*. We thus see that white light is made of different colored lights. Similarly, we can determine what any light is composed of. Every light has its own characteristic spectrum. The light produced by burning sodium, or by introducing a sodium compound in a colorless flame, has a spectrum consisting of a narrow yellow band. The spectrum of potassium consists essentially of two bands, one red and one violet. Further, these bands always occupy definite positions relatively to

one another, so that, on looking through a prism at the light caused by potassium and sodium, the yellow band of sodium is seen in its position, and the two potassium bands in their proper positions.

The instrument used for the purpose of observing the spectra of different lights is called the *spectroscope*. It consists essentially of a prism and two tubes. Through one of the tubes the light to be examined is allowed to pass so as to strike the prism properly. The light emerges from the other side of the prism, and is observed through the other tube, which is provided with lenses for the purpose of magnifying the spectrum. By means of the spectroscope it is possible to detect the minutest quantities of some elements, and, since it was devised, several new elements have been discovered through its aid, as, for example, cæsium, rubidium, thallium, indium, gallium, and others.\*

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\* For an account of the spectroscope and its uses the student is advised to consult some work on physics. The principles involved in its construction are physical principles, and cannot properly be studied in full in a text-book of chemistry.

## CHAPTER XIX.

### THE CALCIUM FAMILY: CALCIUM, BARIUM, STRONTIUM, GLUCINUM.

THE three elements calcium, barium, and strontium resemble one another very closely. Calcium is much more abundant than either of the other members of the family, while strontium is the least abundant of the three. For the present it will be best to confine our attention to the principal member of the family, viz., calcium.

**Calcium, Ca (At. Wt. 40).**—This element occurs very widely distributed in nature, and in enormous quantities. It is found principally as carbonate,  $\text{CaCO}_3$ , in the form of limestone, marble, and chalk; as sulphate,  $\text{CaSO}_4$ , in the form of gypsum; as phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , in phosphorite and apatite; as fluoride,  $\text{CaF}_2$ , in fluor-spar.

The element is made by decomposing calcium chloride by means of the electric current.

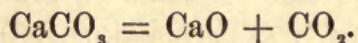
It is a brass-yellow lustrous substance, which in moist air becomes covered with a layer of hydroxide. At ordinary temperatures it decomposes water just as sodium and potassium do.

The principal compounds of calcium with which we have to deal are the *chloride*,  $\text{CaCl}_2$ ; the *oxide*, or quick-lime,  $\text{CaO}$ ; the *hydroxide*, or slaked lime,  $\text{CaO}_2\text{H}_2$ ; the *hypochlorite*,  $\text{Ca}(\text{OCl})_2$ ; the *carbonate*,  $\text{CaCO}_3$ ; the *sulphate*,  $\text{CaSO}_4$ ; the *phosphate*,  $\text{Ca}_3(\text{PO}_4)_2$ ; the *silicate*, in the form of glass.

**Calcium Chloride, CaCl<sub>2</sub>.**—The property which gives this salt its value is its power to absorb water. It is used as a drying agent. Gases are passed through it for the purpose of drying them, and it is also placed in vessels in which it is necessary that the atmosphere should be dry.

**EXPERIMENT 148.**—Dissolve 10 to 20 grams of limestone or marble in ordinary hydrochloric acid. Evaporate to dryness. Expose a few pieces of the residue to the air. [Does it become moist? In what experiments has calcium chloride been used, and for what purposes? What would happen if sulphuric acid were added to calcium chloride?] Try it. Explain what takes place. [Is the residue soluble or insoluble in water?]

**Calcium Oxide, CaO.**—This is the substance commonly called *lime*. It is made by heating calcium carbonate, which is decomposed into lime and carbon dioxide:



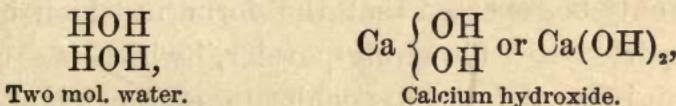
[In what connection have we already met with this reaction?]

Limekilns are large furnaces in which limestone and other forms of calcium carbonate are heated and converted into lime.

[Why is it dangerous to remain for any length of time in the immediate neighborhood of a limekiln?]

Lime is a white, amorphous, infusible substance. When heated in the flame of the compound blow-pipe, it gives forth an intense light, as any other infusible substance would under the same circumstances. When exposed to the air, it attracts moisture and carbon dioxide, and is thus converted into the carbonate. It must hence be protected from the air.

**Calcium Hydroxide,  $\text{CaO}_2\text{H}_2$ .**—When calcium oxide or quick-lime is treated with water it becomes hot and crumbles to a fine powder. The substance which is formed in this operation is somewhat soluble in water, the solution being known as *lime-water*. The chemical change which takes place when lime is treated with water has been explained. It consists in the formation of a compound of the formula  $\text{CaO}_2\text{H}_2$ , and known as slaked lime, and the operation is known as *slaking*. It is believed that just as potassium hydroxide,  $\text{KOH}$ , is properly regarded as water in the molecule of which one atom of hydrogen is replaced by an atom of potassium, so calcium hydroxide is properly regarded as derived from water by the replacement of two atoms of hydrogen in two molecules by one atom of the bivalent metal calcium:



It is difficult to explain to the beginner exactly why this view is held. It can only be said that it is a conception which is in harmony with a great many facts, though it does not follow as a necessary consequence from any facts known to us.

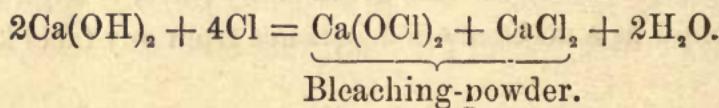
**EXPERIMENT 149.**—To 40 to 50 grams good quick-lime add 100 cc. water. Soon the mass will begin to crumble, and steam will rise from it, indicating that heat is evolved. Afterwards dilute to 2 to 3 litres and put the whole in a well-stoppered bottle. The undissolved lime will settle to the bottom, and in the course of some hours the solution above will become clear. Carefully pour off some of the clear solution. [What takes place when some of the solution is exposed to the air? When the gases from the lungs are

passed through it? When carbon dioxide is passed through it? What takes place when dilute sulphuric acid is added to lime-water? Is calcium sulphate difficultly or easily soluble in water? Has lime-water an alkaline reaction?]

When potassium hydroxide is added to a solution of a salt containing a metal whose hydroxide is insoluble in water, the insoluble hydroxide is precipitated. This was illustrated in Experiments 128 and 129. [What are those experiments?] Calcium hydroxide is a soluble hydroxide, and acts in the same way that potassium hydroxide does.

**EXPERIMENT 150.**—Add some lime-water to a solution of ferric chloride, of copper nitrate, of lead nitrate. Explain the results.

**Calcium hypochlorite**,  $\text{Ca}(\text{OCl})_2$ , has already been considered to a sufficient extent under the head of Chlorine. It need only be repeated that the form in which chlorine is transported is “bleaching-powder,” which is a compound containing calcium hypochlorite and calcium chloride,  $\text{Ca}(\text{OCl})_2 + \text{CaCl}_2$ , made by treating slaked lime with chlorine :



**Calcium Carbonate,  $\text{CaCO}_3$ .**—This salt occurs in nature in the well-known forms calc-spar, limestone, marble, and chalk. The variety of calc-spar found in Iceland, and known as Iceland spar, is particularly pure calcium carbonate.

It crystallizes usually in rhombohedrons, as seen in calc-spar. It is insoluble in water, and is decomposed by acids with evolution of carbon dioxide. The fact that it is solu-

ble in water containing carbon dioxide in solution, and that when such solutions are boiled it is precipitated, has been commented upon. (See Experiment 95.)

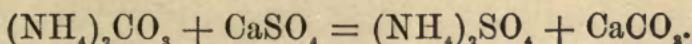
**Calcium Sulphate,  $\text{CaSO}_4 + 2\text{H}_2\text{O}$ .**—Gypsum, the principal natural variety of calcium sulphate, crystallizes with two molecules of water of crystallization,  $\text{CaSO}_4 + 2\text{H}_2\text{O}$ . When heated, it loses its water of crystallization and forms a powder known as *plaster of Paris*, which has the power of taking up water and forming a solid substance. The process of solidification is known as “setting.” Plaster of Paris is largely used in making casts.

Calcium sulphate is somewhat soluble in water. A natural water containing either calcium carbonate or sulphate in solution is called a *hard water*.

It is a curious fact that when anhydrous gypsum, or plaster of Paris, has taken up water to form the compound  $\text{CaSO}_4 + 2\text{H}_2\text{O}$ , the compound differs from gypsum very markedly in one respect. If it be heated, it again loses water; but the anhydrous powder now left has not the power to take up water again.

**EXPERIMENT 151.**—Heat some powdered gypsum to about  $200^\circ$  in an air-bath. Examine the residue and see whether it will become solid when mixed with a little water so as to form a paste.

When gypsum is treated with a solution of the carbonate of an alkali metal, as sodium carbonate or ammonium carbonate, it is completely transformed into the carbonate:

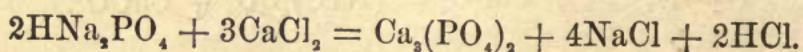


**EXPERIMENT 152.**—Upon a gram or two of powdered gypsum pour, say, 100 cc. of a moderately strong solution

of ammonium carbonate. After a few hours pour off the solution, collect the powder on a filter, and see whether it has changed to the carbonate. [How can you determine whether ammonium sulphate is in solution or not?] Of course, there is still ammonium carbonate present, and this must be taken into account in examining for the sulphate. We usually examine for a sulphate by adding a soluble barium salt, when, if a soluble sulphate is present, barium sulphate is precipitated. In this case, however, the ammonium carbonate would throw down barium carbonate. To prevent this, the ammonium carbonate may first be decomposed by slowly adding sufficient dilute hydrochloric acid. There will then be present ammonium chloride and sulphate; and, now, if barium chloride or any other soluble barium salt be added, barium sulphate will be precipitated.

**Calcium Phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ .**—The normal phosphate in which all the hydrogen of the acid is replaced by calcium is found in nature as phosphorite, and in combination with calcium fluoride or chloride as apatite. It is further the chief inorganic constituent of bones, and is found in large quantity in bone-ash. It is found everywhere in the soil and is taken up by plants. It is formed when a soluble phosphate is added to a solution of a calcium salt.

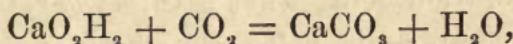
**EXPERIMENT 153.**—To a solution of calcium chloride in a test-tube add disodium phosphate,  $\text{HNa}_2\text{PO}_4$ . The precipitate is calcium phosphate. This salt is decomposed by hydrochloric and nitric acids, and hence dissolves on addition of these acids :



**Monocalcium Phosphate,  $\text{Ca}(\text{H}_2\text{PO}_4)_2 + \text{H}_2\text{O}$ .**—This is

commonly called the acid phosphate. It is formed when ordinary, insoluble calcium phosphate is treated with concentrated sulphuric acid, and is contained in the so-called "superphosphates."

**Mortar.**—Mortar is made of slaked lime and sand. When this mixture is exposed to the air, carbonate of calcium is slowly formed and the mass becomes extremely hard. The water contained in the mortar soon passes off, but nevertheless freshly plastered rooms remain moist for a considerable time. This is due to the fact that a reaction is constantly taking place between the carbon dioxide and calcium hydroxide in which calcium carbonate and water are formed :



and it is the water thus liberated which keeps the air moist. The complete conversion of the lime into carbonate requires a very long time, because the carbonate which is formed on the surface tends to protect the lime in the interior.

**Glass.**—Common glass is a silicate of calcium and sodium, made by melting together sand (silicon dioxide,  $\text{SiO}_2$ ) with lime, or calcium carbonate, and sodium carbonate. When potassium carbonate is used instead of sodium carbonate, the glass is more difficultly fusible. Bohemian glass, which is so extensively used in the manufacture of chemical apparatus, is a silicate of calcium and potassium. Flint-glass, which has a high refractive power, and is hence especially valuable for the manufacture of optical instruments, contains lead instead of calcium. It is much more easily fusible than calcium glass.

Colors are given to glass by putting in the fused mass

small quantities of various substances. Thus a cobalt compound makes glass blue; copper and chromium make it green; one of the oxides of copper makes it red, etc.

The compounds of barium and strontium closely resemble those of calcium. Barium forms an oxide,  $\text{BaO}$ , corresponding to lime, and also another one known as barium dioxide,  $\text{BaO}_2$ .\* This is formed by passing oxygen or air over barium oxide heated to a dull red heat. At a higher temperature it gives off the oxygen. These facts have recently been utilized for the purpose of extracting oxygen from the air.

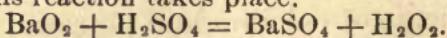
Barium oxide is converted into the hydroxide  $\text{BaO}_2\text{H}$ , when treated with water. This hydroxide is soluble in water, the solution being what is called *baryta-water*.

Calcium compounds color the flame reddish yellow; strontium compounds, intense red; and barium compounds, yellowish green.

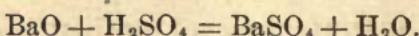
Between the atomic weights of calcium, strontium and barium there exists the same relation as that with which we are already familiar in other families. The atomic weight of calcium is 40; of strontium, 87.5; and of barium, 137:

$$\frac{40 + 137}{2} = 88.5.$$

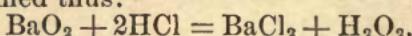
\* This compound has already been referred to in describing the preparation of hydrogen dioxide,  $\text{H}_2\text{O}_2$ . When it is treated with sulphuric acid this reaction takes place:



When barium oxide,  $\text{BaO}$ , is treated with sulphuric acid this reaction takes place:



When barium dioxide is treated with hydrochloric acid, hydrogen dioxide is also formed thus:



[Compare this with the action which takes place when hydrochloric acid acts upon manganese dioxide.]

## CHAPTER XX.

### THE MAGNESIUM FAMILY : MAGNESIUM, ZINC, CADMIUM.

OF the three members of this family, magnesium and zinc are by far the best known.

**Magnesium, Mg (At. Wt. 24).**—Magnesium occurs very widely distributed in nature, and in considerable quantities. Among the important magnesium minerals are *magnesite*, which is the carbonate  $MgCO_3$ ; *dolomite*, a double carbonate of magnesium and calcium; *soapstone*, *serpentine*, and *meerschaum*, which is essentially a silicate of magnesium. Further, there are many silicates which contain magnesium, among them being *asbestos* and *hornblende*. The metal is also found in solution in many spring-waters as the sulphate, or Epsom salt.

It is prepared by treating magnesium chloride with sodium at a high temperature.

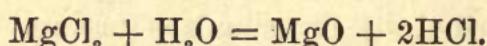
It is a silver-white metal with a high lustre. In the air it changes only slowly, but gradually becomes covered with a layer of the oxide. When heated above its melting-point in the air it burns with a bright flame, forming the white oxide. The light of the flame is very efficient in producing certain chemical changes, as the combination of hydrogen and chlorine. At ordinary temperatures magnesium does not decompose water; at  $100^\circ$  it decomposes it

slowly. [Note the marked difference in this respect between magnesium and the alkali metals.]

The chief compounds of magnesium are the *oxide*,  $MgO$ . called *magnesia*; the *sulphate*,  $MgSO_4 + 7H_2O$ , commonly called Epsom salt; the *carbonate*,  $MgCO_3$ ; the *silicates*; and the *chloride*,  $MgCl_2$ .

**Magnesium Oxide,  $MgO$ .**—This compound is commonly called *magnesia*. A fine white variety is made by heating precipitated magnesium carbonate; it is called *magnesia usta*. It is very difficultly soluble in water, forming with it magnesium hydroxide,  $MgO \cdot H_2O$ , which is practically insoluble in water. [What difference is there between magnesium and calcium in this respect?]

**Magnesium chloride,  $MgCl_2$ ,** is of special interest for the reason that it is the compound from which the metal magnesium is made. It is prepared by dissolving the carbonate in hydrochloric acid. On evaporating this solution to the proper concentration, crystals of magnesium chloride containing water of crystallization,  $MgCl_2 + 6H_2O$ , are deposited. When this compound is heated for the purpose of drying it, the larger part of it undergoes decomposition, thus :



The same thing takes place to some extent on heating calcium chloride with water, so that fused calcium chloride is always slightly alkaline in consequence of the presence of lime, or calcium oxide.

**Zinc, Zn (At. Wt. 65).**—Zinc occurs in nature in combination as the *carbonate*, or *calamine*,  $ZnCO_3$ , and as the *sulphide*, or *zinc blende*,  $ZnS$ .

It is prepared by mixing the oxide with charcoal and

heating in earthenware retorts. The metal, being volatile, passes over and is condensed.

Zinc has markedly different properties at different temperatures. At ordinary temperatures it is quite brittle; at  $100\text{--}150^\circ$  it can be rolled out in sheets, but above  $200^\circ$  it becomes brittle again. In dry air it does not change. When heated in the air it takes fire, and burns with a bluish flame, forming zinc oxide. This has been seen in the experiments with the oxyhydrogen blow-pipe. It dissolves in all the common acids, usually with an evolution of hydrogen. In the case of nitric acid, however, the hydrogen acts upon the nitric acid, reducing it.

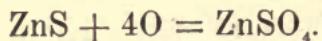
Iron is sometimes covered with a layer of zinc. Thus prepared, it forms what is known as *galvanized iron*. Zinc is a constituent of *brass*.

**Zinc oxide,  $\text{ZnO}$ ,** is obtained as *Flores zinci* by burning zinc, and by heating the carbonate or nitrate of zinc. It turns yellow when heated, but on cooling becomes white again.

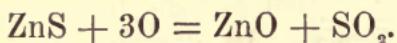
**EXPERIMENT 154.**—Heat a small piece of zinc on charcoal in the oxidizing flame of the blow-pipe. The white fumes of zinc oxide (philosopher's wool) will be seen, and the charcoal will be covered with a film which is yellow while hot, but becomes white on cooling. [What element gives a film which is white both when hot and when cold?]

Zinc oxide is used as a constituent of paint under the name of *zinc white*.

**Zinc Sulphate,  $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ ,** is commonly called white vitriol. [In what experiments has zinc sulphate been obtained?] It is obtained on the large scale by heating zinc sulphide in contact with the air. Under these circumstances, the sulphide is oxidized :

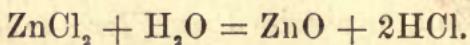


This operation is known as *roasting*. By roasting zinc sulphide at a higher temperature it is converted into zinc oxide :



Zinc sulphate is also formed in large quantities in galvanic batteries and in the preparation of hydrogen.

**Zinc chloride**,  $\text{ZnCl}_2$ , is obtained by evaporating a water solution of the substance and distilling the residue. It is an oily liquid which has a very strong affinity for water. On evaporating a water solution a part of the chloride undergoes decomposition, just as magnesium chloride does, forming the oxide



The hydroxide, sulphide, carbonate, and phosphate of zinc are insoluble in water.

**EXPERIMENT 155.**—Produce the insoluble compounds just mentioned and express the reactions by means of equations.

[What happens on bringing together solutions of sodium carbonate and zinc sulphate? ammonia and zinc chloride? barium chloride and zinc sulphate? lime-water and zinc sulphate? What color has zinc sulphide? Is it thrown down when the solution contains dilute hydrochloric acid? Try it.]

## CHAPTER XXI.

### THE COPPER FAMILY: COPPER, MERCURY, SILVER.

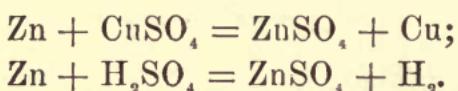
**Copper, Cu (At. Wt. 63.2).**—Copper occurs in nature in the uncombined or native state in large quantities in the neighborhood of Lake Superior, in the United States, and in Chili. It also occurs in combination with oxygen as *ruby copper*, which is the oxide  $\text{Cu}_2\text{O}$ ; and with sulphur and iron in *copper pyrites*.

It is obtained from the oxide by heating it with charcoal. [This reduction has been illustrated under the head of carbon (see Experiment 88).] It is also obtained from the sulphides. The chemical changes involved are comparatively complicated.

Copper is a hard metal of a reddish color and metallic lustre. It does not change in dry air, but in moist air it gradually becomes covered with a green layer of a carbonate of copper. Nitric acid dissolves it, copper nitrate,  $\text{Cu}(\text{NO}_3)_2$ , being formed, and oxides of nitrogen evolved [explain the reaction]; hydrochloric acid does not act upon it; sulphuric acid acts when heated with the metal; the sulphate,  $\text{CuSO}_4$ , is formed and sulphur dioxide given off [explain the reaction]. Copper cannot decompose water, even when water vapor is passed over the metal heated to red heat. [Compare with the conduct of the members of the potassium, calcium, and magnesium families.]

It is precipitated from solutions of its salts by zinc, iron, and some other metals, and by an electric current.

**EXPERIMENT 156.**—Into a neutral solution of copper sulphate insert a strip of zinc. The zinc will become covered with a layer of copper, and zinc will pass into solution as zinc sulphate. The zinc simply displaces the copper in this case, as it displaces hydrogen from sulphuric acid :



Perform a similar experiment, using a strip of sheet-iron instead of the zinc. [What is the result?] To those who first performed this experiment the iron appeared to be changed to copper. [How would you go to work to determine whether the iron is changed to copper or not?]

The deposition of metallic copper from solutions of its salts is extensively utilized in copper-plating. The object to be covered with copper is hung in a solution of copper sulphate and connected with one pole of a galvanic battery, the other pole being also in the solution. Decomposition takes place, and a layer of copper is deposited on the object.

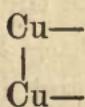
*Brass* is a mixture of 1 part of zinc and 2 parts of copper. *Bell-metal* and *bronze* are mixtures of copper and tin. Such mixtures of metals which are made by melting them together are called *alloys*. It appears that some alloys are closely allied to chemical compounds.

Among the more common compounds of copper are the *oxides*  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ , the *sulphate*  $\text{CuSO}_4$ , and the *sulphide*  $\text{CuS}$ .

Copper has the power to form two distinct series of compounds, of which the following examples will serve as illustrations:

$\text{CuCl}$ ,	$\text{CuCl}_2$ ;
$\text{CuBr}$ ,	$\text{CuBr}_2$ ;
$\text{Cu}_2\text{O}$ ,	$\text{CuO}$ .

Those compounds which are of the first order corresponding to the chloride,  $\text{CuCl}$ , are called *cuprous compounds*. Thus,  $\text{CuCl}$  is *cuprous chloride*;  $\text{Cu}_2\text{O}$ , *cuprous oxide*, etc. On the other hand, compounds of the second order are called *cupric compounds*. Thus,  $\text{CuCl}_2$  is *cupric chloride*;  $\text{CuO}$ , *cupric oxide*, etc. It has been suggested that perhaps the formula of the simpler cuprous compounds like  $\text{CuCl}$ , etc., should be doubled, and written  $\text{Cu}_2\text{Cl}_2$ ,  $\text{Cu}_2\text{Br}_2$ , etc. This suggestion has its origin in the valence conception. In cupric chloride,  $\text{CuCl}_2$ , and cupric oxide,  $\text{CuO}$ , copper is evidently bivalent; whereas if the formulas of the cuprous compounds are the simple ones  $\text{CuCl}$ ,  $\text{CuI}$ , etc., then in them copper is univalent. If, however, cuprous chloride is  $\text{Cu}_2\text{Cl}_2$ , it may be that in it the copper is bivalent. It is only necessary to assume that in the molecule of cuprous chloride two atoms of copper are combined as represented thus :

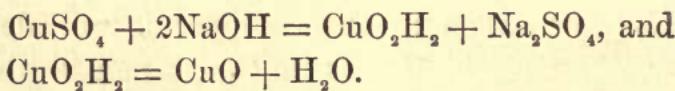


If then each of the copper atoms should combine with a chlorine atom, the compound would have the formula  $\text{Cu}_2\text{Cl}_2$ . Unfortunately, we have no experimental means of showing whether the molecule of cuprous chloride is more probably  $\text{Cu}_2\text{Cl}_2$ , or  $\text{CuCl}$ , so that the above reasoning is purely speculative. It is better, therefore, for the present to keep to the simpler formula. Whatever the

explanation may be, it is unquestionably a fact that there are two series of salts of copper, in one of which there is relatively half as much copper as in the other. Mercury, iron, and some other metals present similar phenomena.

**Cuprous oxide**,  $\text{Cu}_2\text{O}$ , is found in nature as *ruby copper*, and is formed when copper is heated in contact with the air. It is a bright-red insoluble substance.

**Cupric oxide**,  $\text{CuO}$ , is obtained by heating copper to redness in contact with the air, or by heating the nitrate. It is also formed when caustic soda or potash is added to a boiling-hot solution of a copper salt. If the solution is cold, blue *cupric hydroxide*,  $\text{CuO}_2\text{H}_2$ , is precipitated, but this easily loses water, particularly if the solution is heated. The reactions which take place are :



**EXPERIMENT 157.**—Add some caustic soda or potash to a small quantity of a cold solution of copper sulphate in a test-tube. Heat and notice the change from blue to black.

**Copper Sulphate**,  $\text{CuSO}_4 + 5\text{H}_2\text{O}$ .—This salt is manufactured on a large scale and is commonly known by the name “blue vitriol.” [What salt is called “white vitriol?”] It forms large blue crystals, which, when heated, lose water and become colorless. The colorless substance becomes blue again in contact with water.

**Copper Sulphide**,  $\text{CuS}$ , is a black substance which is formed by passing hydrogen sulphide through a solution of a copper salt, or by adding a soluble sulphide, as potassium sulphide or ammonium sulphide to such a solution.

**EXPERIMENT 158.**—Treat a dilute solution of copper sulphate with hydrogen sulphide, with ammonium sulphide, with potassium or sodium sulphide.

**Mercury, Hg (At. Wt. 200).**—Mercury occurs native as drops enclosed in rocks, though principally in combination with sulphur as *cinnabar*,  $HgS$ . It is obtained by roasting cinnabar, when vapors of mercury and sulphur dioxide are given off. The mercury is condensed in appropriate vessels. It is a silver-white metal of a high lustre. At ordinary temperature it is liquid, though it becomes solid at  $-39^{\circ}.5$ . Its specific gravity, water being the standard, is 13.5959. It does not change in the air at ordinary temperatures. It is insoluble in hydrochloric acid and cold sulphuric acid [Try each.] It dissolves in hot concentrated sulphuric acid, and is easily soluble in nitric acid. [Try each.] The vapor of mercury is very poisonous.

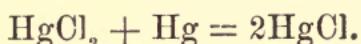
With other metals it forms alloys called *amalgams*. In ordinary galvanic batteries the zinc plates are treated with mercury, and thus covered with a layer of zinc amalgam which protects them from the action of the acids used.

Among the more common compounds of mercury are the oxide,  $HgO$ ; the two chlorides, *mercurous chloride*,  $HgCl$ , and *mercuric chloride*,  $HgCl_2$ ; the two iodides, *mercurous iodide*,  $HgI$ , and *mercuric iodide*,  $HgI_2$ ; and the *sulphide*,  $HgS$ .

**Mercuric oxide,  $HgO$ ,** is the red substance which was used in one of our first experiments for the purpose of preparing oxygen. It is formed when mercury is heated for some time near its boiling-point in contact with the air, and is made by heating the nitrate.

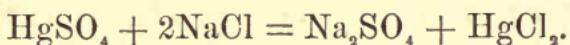
**Mercurous chloride,  $HgCl$ ,** is commonly known by the name *calomel*. It is precipitated when a soluble chloride

or hydrochloric acid is added to a solution of any mercurous salt. It is manufactured by subliming an intimate mixture of mercuric chloride and mercury.



It is a white substance, insoluble in water, which finds extensive application in medicine.

**Mercuric chloride, HgCl<sub>2</sub>**, commonly called *corrosive sublimate*, is manufactured on the large scale by subliming an intimate mixture of mercuric sulphate and common salt:



It is a white substance, soluble in water. It is extremely poisonous, and prevents the decay of organic substances.

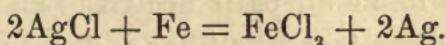
**Mercuric sulphide, HgS**, occurs in nature as cinnabar in the form of *red* crystals or crystalline masses. When prepared artificially by rubbing mercury and flowers of sulphur together or by passing hydrogen sulphide through a solution containing a mercury salt, it is a *black* powder. When sublimed this powder yields red crystals.

It will be noticed that of the two chlorides only mercurous chloride is insoluble in water. If any mercurous salt is present in a solution, mercurous chloride will be thrown down by adding a chloride or hydrochloric acid; whereas if the salt is a mercuric salt the addition of a chloride or hydrochloric acid will produce no precipitate.

**Silver, Ag (At. Wt. 108).**—Silver occurs native; in combination with sulphur; and with sulphur and other metals. Small quantities of silver sulphide are found in almost all varieties of galenite or lead sulphide. It occurs more rarely as the chloride, bromide, and iodide.

Much of the silver in use is obtained from galenite. This mineral is treated in such a way as to cause the separation of the lead (see Lead), and the silver is separated from sulphur at the same time. But it is dissolved in a large quantity of lead, and the problem which presents itself to the metallurgist is how to separate the small quantity of silver from the large quantity of lead. This is accomplished by melting the mixture and allowing it to cool until crystals appear. These are almost pure lead. They are dipped out and the liquid left is again treated in the same way. By this means there is finally obtained a product which is rich in silver but which still contains lead. This is heated in appropriate vessels in contact with the air, when the lead is oxidized, while the silver remains in the metallic state.

Some ores of silver are treated in another way known as the *amalgamation process*. The ores are mixed with common salt and roasted, when the silver is obtained in the form of the chloride. The mass is then treated with iron and water, when this reaction takes place :



The mixture is next treated with mercury, which forms an amalgam with the silver. When this amalgam is heated the mercury passes over, while the silver remains behind.

The methods described above illustrate the applications of chemistry to the solution of important problems.

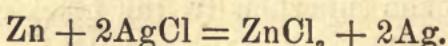
Silver is a white metal with a high lustre. It is not acted upon by air, oxygen, or water. Sulphur acts readily upon it, causing it to blacken superficially, the black coating being silver sulphide. Silver is not dissolved by hydrochloric acid, but is dissolved easily by concentrated sulphuric acid and dilute nitric acid.

The silver which is used for coins and most other purposes is an alloy with copper, the pure metal being too soft. The alloy usually contains from  $7\frac{1}{2}$  to 10 per cent of copper. Other metals covered with a layer of silver, deposited by the action of an electric battery, are said to be silver-plated.

The principal compounds of silver are the *chloride*,  $\text{AgCl}$ ; *bromide*,  $\text{AgBr}$ ; *iodide*,  $\text{AgI}$ ; and *nitrate*,  $\text{AgNO}_3$ .

**Silver nitrate**,  $\text{AgNO}_3$ , is known also by the name "lunar caustic." It is prepared by dissolving silver in dilute nitric acid.

**EXPERIMENT 159.**—Dissolve a ten or twenty-five cent piece in dilute nitric acid. [What action takes place?] Dilute the solution to 200 to 300 cc. with water. [What is the color of the solution? What does this indicate? Does this color prove the presence of copper?] Add a solution of common salt until it ceases to produce a precipitate. [What is the chemical change?] Filter off the white silver chloride and carefully wash with hot water. Dry the precipitate on the filter, by placing the funnel with the filter and precipitate in an air-bath heated to about  $110^\circ$ . Remove the precipitate from the filter and put it into a porcelain crucible. Heat gently with a small flame until the chloride is melted. Cut out a piece of sheet-zinc large enough to cover the bottom of the crucible, and lay it on the silver chloride. Now add a little water and a few drops of dilute sulphuric acid, and let the whole stand for twenty-four hours. The silver chloride is reduced to silver, and zinc chloride is formed :



Take out the piece of zinc and wash the silver with a little dilute sulphuric acid, and then with water. Heat a

small piece of the metal on charcoal with the blow-pipe flame until it melts and forms a bead. Dissolve the silver in dilute nitric acid and evaporate to dryness in the water-bath, so that the excess of nitric acid is driven off. Dissolve the residue in water and put the solution either in a bottle of dark glass or one wrapped in dark paper.

**EXPERIMENT 160.**—To a few cubic centimetres of water in a test-tube add 5 to 10 drops of the solution of silver nitrate just prepared. To this dilute solution add a little of a dilute solution of sodium chloride. The curdy white precipitate is silver chloride. Stand it aside where the light can shine upon it, and notice the change of color which gradually takes place. In the same way make the bromide by adding potassium bromide, and the iodide by adding potassium iodide to silver nitrate.

It will be seen from the last experiments that the chloride, bromide, and iodide of silver are insoluble in water and are changed by light. The art of photography is based upon the changes which certain compounds, especially salts of silver, undergo when exposed to the light. A plate of glass is covered in the dark with a thin layer of a salt of silver. The plate is then exposed in the camera to the action of the light from some object to be photographed. The salt is changed when it is acted upon by the light, while where there is no light it is not acted upon. An image of the object towards which the plate was directed is thus left on the plate.

Silver is precipitated from solutions of its salts by zinc, copper, mercury, and other metals.

**EXPERIMENT 161.**—To a solution of silver nitrate containing about 5 grams of the salt in 100 cc. water add a few drops of mercury, and let it stand. In a few days

the silver will be deposited in the form of delicate crystals. The formation is called the "silver tree."

The oxide, chloride, bromide, iodide, sulphide, carbonate, and phosphate of silver are insoluble in water. [Verify these statements.]

[What takes place when hydrochloric acid is added to a solution of a silver salt? When silver nitrate is added to barium chloride? When ammonium carbonate is added to silver nitrate? When disodium phosphate is added to silver nitrate? In this case, normal silver phosphate,  $\text{Ag}_3\text{PO}_4$ , is formed, and some nitric acid is set free.]

Silver forms mostly those compounds which are analogous to the cuprous and mercurous salts, and not those which are analogous to the cupric and mercuric salts. There is, however, an oxide,  $\text{Ag}_2\text{O}$ , and another,  $\text{AgO}$ , corresponding to mercurous and mercuric oxides.

**The Specific Heat of Elements as a means of Determining their Atomic Weights.**—The question naturally suggests itself, How are the atomic weights determined in the case of elements like silver, copper, etc., which cannot be converted into the form of vapor, and which do not yield compounds which can be converted into vapor? It will be remembered that most of the atomic weights with which we have thus far had to deal, as those of oxygen, chlorine, nitrogen, etc., are determined by a consideration of the specific gravity of the vapors of the compounds of these elements. We determine the relative weights of equal volumes of these gases or vapors, and then, assuming that these weights express the relative weights of the molecules of the compounds, we select the smallest weight of the element occurring in any compound as the atomic weight. [Refer back and carefully read the chapter relating to the

Atomic Theory and Avogadro's Hypothesis.] But however valuable this method may be, it does not help us in the case of solid elements, which cannot be converted into vapor, and which do not yield compounds capable of conversion into vapor. In such cases the effect of heat upon the elements is of assistance. It has been found that when equal weights of different elements are exposed to exactly the same source of heat, they require different lengths of time to become heated to the same temperature. Given exactly the same heating power, it requires 32 times as long to raise the temperature of a pound of water 10, 20, or 30 degrees as it does to raise a pound of mercury the same number of degrees; or it takes 32 times as much heat to raise a pound of water 10, 20, or 30 degrees as it does to raise a pound of mercury the same number of degrees. The quantity of heat required to raise the temperature of a certain weight of a substance one degree as compared with the quantity of heat required to raise the temperature of the same weight of water one degree is called the specific heat of the substance. Thus, from what was said above, the specific heat of mercury is  $\frac{1}{32}$ , or, in decimals, 0.03332. In a similar way it can be shown that the specific heat of gold is 0.03244; of zinc, 0.0955; of silver, 0.057; of copper, 0.0952. But these figures bear a remarkable relation to the combining weights found by means of analysis. Thus, taking the above elements, we have :

	Specific Heat.	Comb. Weight.
Mercury.....	0.03332.....	200
Gold .....	0.03244.....	196.2
Zinc.....	0.0955 .....	65
Silver.....	0.057 .....	108
Copper .....	0.0952.....	63.2

Calculation will show that the specific heat of these elements is approximately inversely proportional to their combining weights. Thus

$$\frac{0.03332}{\text{Sp. Ht. of Hg.}} : \frac{0.057}{\text{Sp. Ht. of Ag.}} :: \frac{108}{\text{Comb. Wt. of Ag.}} : \frac{200}{\text{Comb. Wt. of Hg.}}$$

And the same is true in the other cases. Or the relation may be stated in another way, viz.: The product of the specific heat of any element multiplied by its combining weight is the same in all cases. The product is about 6.25. It is believed that the quantities of the elements to which this law refers are in reality the atomic weights, and we therefore accept the law known as the law of Dulong and Petit, which is this :

*The atomic weight of an element multiplied by its specific heat is a constant equal to about 6.25.*

There are some exceptions to the law, but these cannot be discussed at this time. With its imperfections it is of value, and is now recognized as furnishing a valuable means of determining atomic weights. If A represents the atomic weight, and S the specific heat, then, according to the law of Dulong and Petit,  $A \times S = 6.25$  nearly, and  $A = \frac{6.25}{S}$ . By determining the specific heat of an element, and dividing it into 6.25, a figure will be obtained near the atomic weight. By careful analysis of compounds of the element the figure can be determined more accurately.\*

\* The mere committal to memory of the rule  $A = \frac{6.25}{S}$  without an understanding of the facts from which it is deduced is of no value. In the early stages of his course in chemistry the student should not be allowed to repeat the rule without a careful statement in his own words of its meaning.

## CHAPTER XXII.

THE ALUMINIUM FAMILY: ALUMINIUM, GALLIUM, INDIUM, THALLIUM, SCANDIUM, YTTRIUM, LANTHANUM, AND YTTERBIUM.

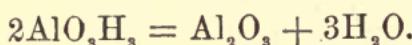
THE only element of this family which need be considered now is aluminium. This is an extremely important element, which occurs very widely distributed in nature.

Aluminium, Al (At. Wt. 27).—Among the many important and widely distributed minerals which contain aluminium are feldspar, granite, mica, and cryolite. Clay is aluminium silicate.

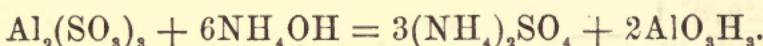
Aluminium is prepared by treating the chloride with metallic sodium. [How is magnesium prepared? How sodium?] Its color is like that of tin, and it has a strong lustre. It is very strong and yet malleable. It is lighter than most metals in common use, its specific gravity being 2.7, while that of iron is 7.8, that of silver 10.57, and that of tin 7.3. Further, it does not change in dry or moist air. These properties give it great value, and it is only the fact that it cannot be prepared cheaply from the compounds found in nature that prevents its wide-spread use. The discovery of a method by which aluminium could be prepared economically would be of the highest importance. It will only be made through a thorough study of the laws of chemistry, and will come with a clearer understanding of the science. Among the more important compounds of aluminium are *aluminium oxide*,  $\text{Al}_2\text{O}_3$ ; *aluminium hydroxide*,  $\text{AlO}_3\text{H}_2$ ; the *alums*; the *silicates*; and the *chloride*,  $\text{Al}_2\text{Cl}_6$  or  $\text{AlCl}_3$ .

Aluminium Oxide,  $\text{Al}_2\text{O}_3$ .—This compound occurs rarely in nature in the form of ruby, sapphire, and corundum.

It is very hard, and as *emery* is used for polishing. It is made artificially by heating the hydroxide,  $\text{AlO}_3\text{H}_3$ :



**Aluminium Hydroxide,  $\text{AlO}_3\text{H}_3$ .**—This compound is found in nature in crystallized form as hydrargillite. It is precipitated when ammonia is added to a solution of aluminium sulphate:

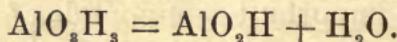


It forms a gelatinous mass which is difficult to filter.

[Precipitate some from a solution of ordinary alum.] The hydroxide is soluble in acids and in alkalies. In the former case salts are formed in which the hydroxide plays the part of a base; in the latter it acts like an acid. The salts formed with the alkalies are called *aluminates*. In aluminium salts one atom of the metal replaces three atoms of hydrogen; thus, aluminium nitrate is  $\text{Al}(\text{NO}_3)_3$ ; the sulphate,  $\text{Al}_2(\text{SO}_4)_3$ , etc. In the aluminates the three hydrogen atoms of the hydroxide are replaced by metal; thus, potassium aluminate is  $\text{AlO}_3\text{K}_3$ , and sodium aluminate,  $\text{AlO}_3\text{Na}_3$ .

**EXPERIMENT 162.**—Precipitate some aluminium hydroxide from a dilute solution of alum, by means of caustic potash, and continue to add the latter slowly, when the precipitate will dissolve. Do the same with caustic soda.

Aluminium hydroxide,  $\text{AlO}_3\text{H}_3$ , loses water when heated, and a compound of the formula  $\text{AlO}_2\text{H}$  is formed:



This compound is found in nature as the mineral dia-spore. It has acid properties and forms extremely stable salts, several of which are found in nature. Spinel is

magnesium aluminate ( $\text{AlO}_2\text{Mg}$ ). The formation of the hydroxides  $\text{AlO}_2\text{H}$ , and  $\text{AlO}_2\text{H}$ , and of salts derived from each, indicates some analogy between aluminium and boron. On the other hand, the power to replace the hydrogen of acids is not possessed by boron. [Refer back to Boron. Read again what is said about it, and note particularly the points of resemblance and difference with aluminium.]

**Alums.**—Aluminium sulphate forms complex compounds with the sulphates of the alkali metals, all of which crystallize beautifully. Potassium alum is the best known of these. It may be regarded as derived from 2 molecules of sulphuric acid by the replacement of 3 atoms of hydrogen by 1 atom of aluminium, and the fourth by 1 atom of potassium; thus,  $\text{AlK}(\text{SO}_4)_2$ . The crystals always contain 12 molecules of water, the complete formula being  $\text{AlK}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ . Similarly, sodium alum is  $\text{AlNa}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ , and ammonium alum  $\text{AlNH}_4(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ .

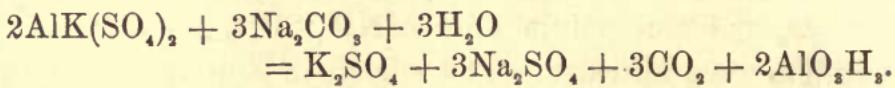
**Aluminium Silicates.**—The silicate of aluminium occurs in nature in enormous quantities, in combination with other silicates forming some of the most important minerals. The most abundant of these is ordinary feldspar, which is a silicate of aluminium and potassium,  $\text{AlKS}_i\text{O}_8$ . Clay, which in pure form is known as *Kaoline*, is aluminium silicate in combination with water,  $\text{Al}_4(\text{SiO}_4)_3 + 4\text{H}_2\text{O}$ . It is derived from the acid  $\text{H}_4\text{SiO}_4$ . Kaoline is used for making porcelain. Ordinary clay is used for making bricks and for other purposes.

**Ultramarine.**—The substance known as *lapis lazuli* consists of a silicate of aluminium and sodium, together with a polysulphide of sodium. The coloring matter obtained by powdering it was formerly very expensive, but it is now made artificially by the ton, and the color of the artificially

prepared substance is even more beautiful than that of the natural.

With weak acids aluminium forms no salts. There is, for example, no carbonate. The sulphide is so unstable that it decomposes into the hydroxide and hydrogen sulphide when exposed to moist air. When a soluble hydroxide is added to a solution of a salt of aluminium, the insoluble hydroxide is precipitated; but, as this has acid properties, it is dissolved in an excess of either caustic soda or caustic potash. Owing to the weak basic properties of the hydroxide, sodium carbonate and other soluble carbonates precipitate, not the carbonate, but the uncombined hydroxide.

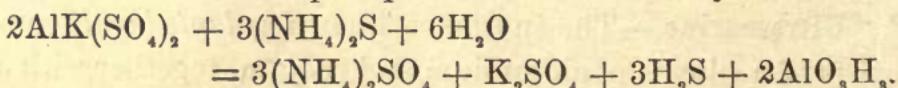
**EXPERIMENT 163.**—Add a dilute solution of sodium carbonate to a dilute solution of alum. The precipitate is the hydroxide:



Filter off and show that the precipitate is not the carbonate. Try the same experiment with ammonium and potassium carbonates.

When an aluminium salt in solution is treated with ammonium sulphide, the hydroxide is precipitated. Even if the sulphide were formed it would be decomposed into the hydroxide and hydrogen sulphide by water.

**EXPERIMENT 163 a.**—Add ammonium sulphide to a solution of alum. The precipitate is aluminium hydroxide:



The other members of the aluminium family need not be considered here. Two of them, gallium and scandium, have only recently been discovered.

## CHAPTER XXIII.

### THE IRON FAMILY : IRON, COBALT, NICKEL.

**Iron, Fe (At. Wt. 56).**—At the present time it is undoubtedly true that iron is the most important metal for man. It is not improbable, however, that in the future aluminium may take its place for many purposes, though there appears to be no immediate prospect of this interference with the iron industry.

Iron occurs in the form of the oxides,  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ; as the carbonate,  $\text{FeCO}_3$ ; in combination with sulphur as iron pyrites,  $\text{FeS}_2$ ; and as silicates and hydrated oxides, or hydroxides.

The extraction of iron from its ores is theoretically simple, the essential steps in the process being :

(1) The conversion of the ore into the oxides, unless the oxides are themselves found.

This is accomplished by *roasting* them. If sulphides are roasted the sulphur passes off as sulphur dioxide, and the iron remains as the oxide. In roasting, further, water is driven off and the carbonate is decomposed into oxide and carbon dioxide.

(2) Reduction of the oxides by means of charcoal or coke.

This is accomplished by mixing the ore with the reducing agent and heating in a blast-furnace. As the iron is reduced it sinks into the lower part of the furnace, which is called the crucible, and is drawn off in the liquid condition.

The iron drawn off from the crucible is called *pig-iron*. It is always impure, containing carbon, phosphorus, sulphur, silicon, etc. In this condition it is brittle and easily fusible. It is used for casting, and is known as *cast iron*. When the carbon, silicon, and phosphorus are removed the iron is very tough and malleable. This is *wrought iron*. Cast iron is converted into wrought iron in one of two ways :

(1) By melting it and blowing air into the molten mass. The carbon, phosphorus, and silicon are thus oxidized and gotten rid of. This process is known as *puddling*.

(2) By mixing cast iron with some of the purer ores and heating to a high temperature, when the carbon, phosphorus, etc., are oxidized by the oxygen of the ores. This process is called *cementation*.

**Steel** contains more carbon than wrought and less than cast iron. There are two methods by which it is made :

(1) Wrought iron is heated with charcoal or with iron containing carbon. This is known as the *cementation* process.

(2) Cast iron is melted in a large vessel called a converter, and then partly oxidized by currents of air forced into the mass. Cast iron is now added, and steel containing any desired proportion of carbon thus made. This is known as the Bessemer process.

The differences between cast iron, wrought iron, and steel are very marked. They may be summed up in a few words as follows :

Cast iron melts easily, is brittle when cold, and is not as hard as steel.

Steel has the property of becoming extremely hard and brittle, when heated and suddenly cooled. When cau-

tiously heated and allowed to cool slowly it is rendered elastic. This process is called tempering.

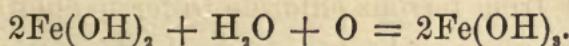
Wrought iron is tough and malleable.

Pure iron is almost unknown. It is a white metal. In moist air it *rusts*; that is, it becomes covered with a layer of oxide and hydroxide which is formed by the action of the air and water.

Iron, like mercury and copper, forms two series of compounds which differ markedly from each other. These are the *ferrous* and *ferric* compounds. Thus with chlorine it forms two chlorides, one of which, *ferrous chloride*, has the composition expressed by the formula  $\text{FeCl}_2$ ; the other, *ferric chloride*, by  $\text{FeCl}_3$ . It appears from a study of the specific gravities of the vapors of these chlorides that the above formulas should be doubled, so that ferrous chloride is now commonly represented by  $\text{Fe}_2\text{Cl}_4$ , and ferric chloride by  $\text{Fe}_2\text{Cl}_6$ .

Similarly there are two oxides,  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$ ; two sulphates, *ferrous sulphate*,  $\text{FeSO}_4$ , and *ferric sulphate*,  $\text{Fe}_2(\text{SO}_4)_3$ , etc.

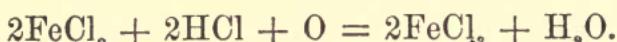
Ferrous compounds show a tendency to pass into ferric compounds by simple contact with the air; and are readily converted by oxidizing agents, such as nitric acid, potassium chlorate, etc. When, for example, ferrous hydroxide,  $\text{Fe}(\text{OH})_2$ ,\* is exposed to the air suspended in water, it changes to ferric hydroxide,  $\text{Fe}(\text{OH})_3$ . The change is represented by the equation




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\* If ferrous chloride has the formula  $\text{Fe}_2\text{Cl}_4$ , it seems probable that the formula of ferrous hydroxide is  $\text{Fe}_2(\text{OH})_4$ . We have no evidence in regard to this, and hence the simpler formula may be used here, particularly as we are for the present interested mainly in the composition of the compound.

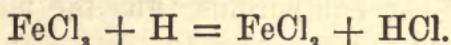
So, also, when ferrous chloride is left standing in hydrochloric acid solution it changes to ferric chloride, and the change is rapidly effected by boiling with a little nitric acid:



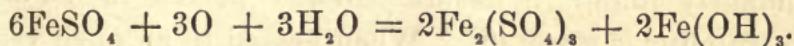
Ferrous chloride,  $\text{FeCl}_2$ , is formed by dissolving iron in hydrochloric acid.

**EXPERIMENT 164.**—Dissolve a little iron wire in dilute hydrochloric acid. Hydrogen is evolved, accompanied by small quantities of other gases, whose formation is due to the presence of impurities in the iron, and carbon is left undissolved as a black residue. To a little of the solution in a test-tube add at once caustic soda. This precipitates ferrous hydroxide,  $\text{Fe(OH)}_2$ , which changes color rapidly, becoming reddish-brown finally. Pure ferrous hydroxide is white. As it passes to the ferric condition it becomes dirty-green, and darker and darker until it is reddish-brown. Heat another portion of the solution of ferrous chloride to boiling, add two or three drops of concentrated nitric acid, and boil again. Repeat this operation two or three times. The ferrous chloride is thus oxidized to ferric chloride. It will be noticed that the color of the solution after the oxidation is reddish-yellow, whereas before the oxidation it was nearly colorless or greenish. Add caustic soda to the solution of ferric chloride. A reddish-brown precipitate of ferric hydroxide will be formed. Just as in this case we have passed from ferrous chloride to ferric chloride by oxidation, so we can pass back again to the ferrous compound. Thus, by adding a little zinc to a solution of ferric chloride in which hydrochloric acid is present, the hydrogen evolved

extracts chlorine from the ferric chloride and converts it into ferrous chloride:



**Ferrous Sulphate,  $\text{FeSO}_4 + 7\text{H}_2\text{O}$ .**—This salt, which is commonly known as “green vitriol” or “copperas,” is formed by the action of sulphuric acid on iron. [What is “white vitriol,” “blue vitriol?”] It undergoes change in the air, being converted into a compound containing ferric sulphate,  $\text{Fe}_2(\text{SO}_4)_3$ , and ferric hydroxide:



**Iron alum,  $\text{FeK}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ ,** is formed by bringing ferric sulphate and potassium sulphate together. It resembles ordinary alum,  $\text{AlK}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ , but differs from it in containing iron instead of aluminium.

**Ferrous oxide,  $\text{FeO}$ ,** cannot be prepared in pure condition on account of its great affinity for oxygen.

**Ferric oxide,  $\text{Fe}_2\text{O}_3$ ,** occurs in nature in lustrous crystals as *haematite*, and in other valuable ores of iron. The hydroxide corresponding to this—viz., *ferric hydroxide*,  $\text{Fe(OH)}_3$ —is analogous in composition and properties to aluminium hydroxide. It is a weak base, but, unlike aluminium hydroxide, it does not form compounds with bases. Hence it does not dissolve in caustic soda and caustic potash. [Try it. Suppose a solution contains an aluminium salt and a ferric salt, and caustic soda be added, what will first take place? If more be added and the solution filtered, where will the aluminium be found, and where the iron?]

**Ferroso-ferric oxide,  $\text{Fe}_3\text{O}_4$ ,** or magnetic oxide of iron, is found in nature in the form of loadstone. It is formed when iron is burned in oxygen (see Experiment 25).

**Ferric Acid,  $H_2FeO_4$ .**—It is interesting to note that iron combines with a larger proportion of oxygen than is contained in any of the compounds thus far mentioned, and then forms an acid. Potassium ferrate has the composition represented by the formula  $K_2FeO_4$ .

The *sulphides* of iron have been repeatedly mentioned. **Ferrous sulphide**,  $FeS$ , is made by heating sulphur and iron together in proper proportions. It is used in making hydrogen sulphide [explain how].

**Iron pyrites,  $FeS_2$ ,** is a yellow crystallized substance very abundantly found in nature. When heated in a closed tube, sulphur is given off. When heated in an open vessel as upon a shallow iron pan, the sulphur is oxidized to sulphur dioxide, and the iron is left in the form of the oxide. [Verify these statements by experiment.]

**Nickel, Ni (At. Wt. 58.5)**, is found in meteoric iron and in combination with arsenic. It forms two series of salts corresponding to the two hydroxides nickelous hydroxide,  $Ni(OH)_2$ , and nickelic hydroxide,  $Ni(OH)_3$ .

Most nickel salts are colored green.

**Cobalt, Co (At. Wt. 59.1)**, is found in combination with arsenic and sulphur, and also in small quantities accompanying nickel in meteoric iron.

## CHAPTER XXIV.

### MANGANESE.—CHROMIUM.—URANIUM.—BISMUTH.

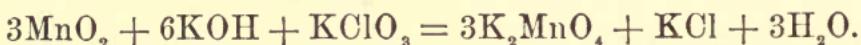
**Manganese, Mn (At. Wt. 55).**—Manganese is found in nature in the form of oxides, of which manganese dioxide, or the black oxide of manganese, occurs most frequently. With oxygen it forms the following compounds: *manganous oxide*,  $MnO$ ; *manganic oxide*,  $Mn_2O_3$ ; *manganoso-manganic oxide*,  $Mn_3O_4$ ; *manganese dioxide*,  $MnO_2$ ; and *permanganic anhydride*,  $Mn_2O_7$ .

Manganese presents points of resemblance with aluminium and iron. Like iron it forms two series of salts, the manganous and manganic series, which differ from each other very much as ferrous and ferric salts do. Like iron, also, it forms an oxide,  $Mn_3O_4$ , which is analogous to the magnetic oxide of iron. Unlike iron, it forms the dioxide  $MnO_2$ . Like iron, it forms salts, which are derived from an acid of the formula  $H_2MnO_4$ ; as, for example, *potassium manganate*,  $K_2MnO_4$ . Unlike iron, it forms salts derived from an acid  $HMnO_4$ ; as, for example, *potassium permanganate*,  $KMnO_4$ .

All the higher oxides of manganese lose a part of their oxygen very easily, and are usually converted into manganous salts, like  $MnSO_4$ ,  $MnCl_2$ , etc., in which the metal is apparently bivalent. The use of manganese dioxide in preparing oxygen and chlorine has been described. [Give an account of the changes which manganese dioxide un-

dergoes when treated with sulphuric acid; hydrochloric acid; when heated.]

**Potassium Permanganate,  $KMnO_4$ .**—This salt is obtained from potassium manganate,  $K_2MnO_4$ , by boiling or by passing carbon dioxide into it. The manganate is made by treating manganese dioxide with potassium hydroxide and potassium chlorate; in other words, by oxidizing manganese dioxide in the presence of the base, potassium hydroxide. The reaction is represented by the equation



The permanganate is a dark-colored, crystallized compound which dissolves in water, forming a deep-purplish red-colored solution.

**EXPERIMENT 165.**—In a small porcelain crucible heat together 5 grams manganese dioxide,  $MnO_2$ , 5 grams solid potassium hydroxide, and  $2\frac{1}{2}$  grams potassium chlorate,  $KClO_3$ . When the mass has turned green, dissolve the contents in water and boil the solution. The green substance is potassium manganate. The color will change from green to purple.

Potassium permanganate gives up its oxygen very readily and changes to a lower hydroxide. If an acid is present the hydroxide dissolves, forming a colorless solution. When, therefore, a solution of potassium permanganate is added to an acid solution containing an oxidizable substance it becomes colorless.

**EXPERIMENT 166.**—To a dilute solution of ferrous sulphate containing free sulphuric acid add drop by drop a dilute solution of potassium permanganate. The color will disappear as long as there is any unchanged ferrous sulphate present.

Add some permanganate solution to a solution of sulphur dioxide in water. [What would you expect to take place in this case?]

Add some comparatively dilute hydrochloric acid to a few crystals of potassium permanganate in a test-tube. [What do you notice? How do you explain the change?]

Potassium permanganate,  $KMnO_4$ , is analogous to potassium perchlorate,  $KClO_4$ , not only in composition, but in its general properties.

Chromium, and the rare elements molybdenum, tungsten, and uranium resemble one another sufficiently to justify us in grouping them together. For the present we may confine our attention to chromium and uranum.

**Chromium, Cr (At. Wt. 52.3).**—This element is comparatively rare, and occurs almost only in combination with oxygen and iron as chromic iron. This mineral, whose composition is represented by the formula  $FeCr_2O_4$ , may be regarded as the iron salt of an acid of the formula  $HCrO_2$ . Replacing two atoms of hydrogen of this acid by one of iron, we would have a compound  $Fe(CrO_2)_2$ . This is analogous to spinel, which in a similar way is regarded as a magnesium aluminate of the formula  $Mg(AlO_2)_2$ . The principal compounds of chromium with which we have to deal are *potassium chromate*,  $K_2CrO_4$ ; *potassium dichromate*,  $K_2Cr_2O_7$ , and other salts derived from chromic acid. There are, however, salts in which chromium takes the part of a metal, replacing the hydrogen of acids; as, for example, *chromium sulphate*,  $Cr_2(SO_4)_3$ .

Potassium chromate,  $K_2CrO_4$ , is formed when finely powdered chromic iron is heated with potassium carbonate and potassium nitrate.

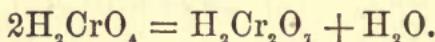
**EXPERIMENT 167.**—Powder some chromic iron very

finely. Mix 3 grams with 3 grams each of potassium carbonate and potassium nitrate. Heat to fusion for some time in a porcelain crucible. After cooling treat the mass with water, when a yellow-colored solution will be formed. Potassium chromate,  $K_2CrO_4$ , is in the solution. Save this solution.

**Potassium Dichromate,  $K_2Cr_2O_7$ .**—This is the form in which chromium is most frequently met with. It is formed from the chromate by adding acetic or nitric acid. The change which takes place is represented thus :



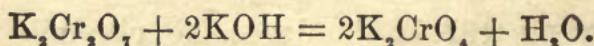
The relation between the chromate and the dichromate will be more readily understood by considering the acids from which they are derived. These are chromic acid,  $H_2CrO_4$ , and dichromic acid,  $H_2Cr_2O_7$ . The latter may be regarded as derived from the former by loss of water:



The same relation exists between sulphuric acid,  $H_2SO_4$ , and disulphuric or fuming sulphuric acid,  $H_2S_2O_7$ .

**EXPERIMENT 168.**—To the solution of potassium chromate already obtained add nitric acid enough to decompose the unused potassium carbonate and give the solution an acid reaction. The color will change from yellow to red. The red color indicates the presence of the dichromate.

When a solution of potassium dichromate is treated with potassium hydroxide until the color becomes pure yellow, the chromate is formed:



**EXPERIMENT 169.**—Convert 10 to 20 grams potassium dichromate into the chromate by the method mentioned. Evaporate to crystallization.

Potassium dichromate forms large red crystals, which are soluble in water.

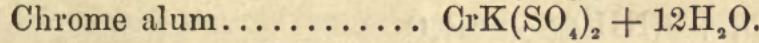
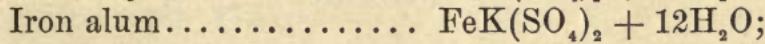
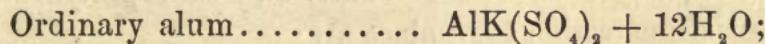
Both the chromate and the dichromate are good oxidizing agents.

**EXPERIMENT 170.**—Treat a little of each salt in a test-tube with hydrochloric acid. [What evidence do you get that the salts are good oxidizing agents ?]

The chromates, like the sulphates of barium and lead, are insoluble in water. They are yellow. The lead salt is the well-known pigment *chrome-yellow*.

**EXPERIMENT 171.**—Add a little of a solution of potassium chromate or dichromate to a solution of a barium salt, and of a lead salt.

Chrome alum is a salt allied to ordinary alum, but containing chromium instead of aluminium. Its formula is  $\text{CrK}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ . The alums have analogous formulas:

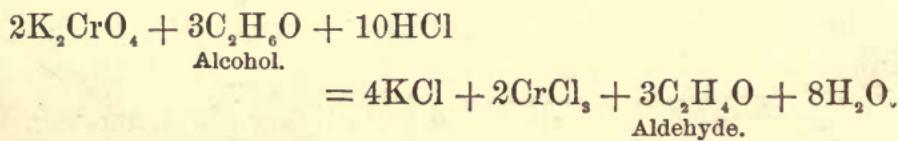


In its general chemical conduct chromium is similar to aluminium and iron on the one hand; while, on the other hand, its resemblance to sulphur is unmistakable, as is seen in the formation of the acids, chromic and dichromic acids, which are analogous to sulphuric and disulphuric acids, not only in composition, but in some of their properties. [Are the lead and barium salts of sulphuric acid soluble or insoluble in water ?]

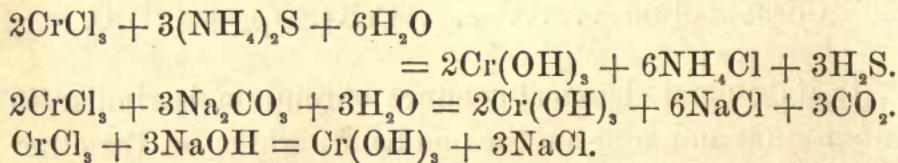
In its conduct towards reagents chromium more closely

resembles aluminium than iron. It forms no sulphide and no carbonate, so that when a soluble carbonate or sulphide is added to a solution of a chromium salt, such as chrome alum, the hydroxide is precipitated, as in the case of aluminium. The hydroxide dissolves in caustic soda and caustic potash, but is reprecipitated when the solution is boiled. [How do aluminium and iron hydroxides act towards caustic soda ?]

**EXPERIMENT 172.**—To a solution of potassium chromate add some hydrochloric acid and a little alcohol. On boiling the alcohol takes up oxygen from the chromate, a peculiar smelling substance, aldehyde, is given off, and the solution now contains chromium chloride,  $\text{CrCl}_3$ . The solution has a green color. The change is represented thus:



To separate portions of the diluted solution add ammonium sulphide, sodium carbonate, and sodium hydroxide. The reactions which take place are:



After noticing the general appearance of the precipitate formed with caustic soda, add an excess of the latter. [Does the precipitate dissolve ? How is this explained ?] Boil the solution. [What takes place ? How is this explained ?]

**Uranium, U (At. Wt. 239).**—This element occurs mostly in the form of the oxide  $\text{U}_2\text{O}_4$ , known as pitchblende. It

forms salts in which the group  $\text{UO}_2$ , called *uranyl*, takes the place of one atom of hydrogen; as, for example, *uranyl nitrate*,  $(\text{UO}_2)\text{NO}_3 + 3\text{H}_2\text{O}$ ; *uranyl sulphate*,  $(\text{UO}_2)\text{SO}_4 + 3\text{H}_2\text{O}$ .

Uranium oxide,  $\text{U}_2\text{O}_5$ , conducts itself towards bases like an acid, forming salts called *uranates*.

Just as manganese is in some respects analogous to the members of the chlorine family [in what respects ?], and chromium in some respects resembles the members of the sulphur family [in what respects ?], so there is an element which, although usually acting the part of a metal, is in some respects similar to the members of the nitrogen family. This is bismuth.

**Bismuth, Bi (At. Wt. 208)**, occurs mostly native, and is obtained by heating the ores and allowing the molten bismuth to run out. In appearance it closely resembles antimony.

The chief compound of bismuth and oxygen is the yellow oxide  $\text{Bi}_2\text{O}_3$ . This is formed when bismuth is burned in the air. If burned on charcoal a yellow film is formed.

**EXPERIMENT 173.**—Heat a small piece of bismuth on charcoal, and notice the yellow film. [What other metal which we have studied forms a yellow film ? What difference is there between it and the film caused by bismuth ?]

The principal salt of bismuth is the nitrate  $\text{Bi}(\text{NO}_3)_3 + 5\text{H}_2\text{O}$ .

**Bismuth sulphide,  $\text{Bi}_2\text{S}$** , occurs in nature, and is formed by passing hydrogen sulphide through a solution of a bismuth salt. It is a black substance.

Bismuth forms two classes of salts which are known as the *bismuth* and *bismuthyl* salts. In the former bismuth acts as a trivalent metal, taking the part of three atoms of

hydrogen, as in the nitrate,  $\text{Bi}(\text{NO}_3)_3$ ; in the latter, the group bismuthyl,  $\text{BiO}$ , takes the place of one atom of hydrogen, as in bismuthyl nitrate,  $\text{BiO}(\text{NO}_3)$ . Antimony forms similar salts.

[What takes place when sodium hydroxide is added to a solution of a calcium salt? a barium salt? a magnesium salt? a zinc salt? an aluminium salt? a ferrous salt? a ferric salt? a chromium salt? a copper salt? What takes place when sodium carbonate is added to each of these salts? when sulphuric acid is added? when hydrogen sulphide is passed through the solutions?]

## CHAPTER XXV.

### THE LEAD FAMILY: LEAD, TIN.—PLATINUM, GOLD.

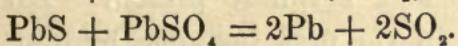
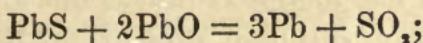
THE only two members of this family which we need consider here are lead and tin. It must be confessed that the resemblance between these elements is not very striking, though there are some points of resemblance.

**Lead, Pb (At. Wt. 207).**—Lead occurs in combination in several forms in nature, as, for example, in the sulphate, carbonate, chromate, and sulphide. The sulphide, PbS, known as galenite, is the most important source of lead. The extraction of the metal from the sulphide is accomplished in one of two ways:

(1) By heating the sulphide with iron, when the latter combines with the sulphur, forming iron sulphide, while the lead is set free.

(2) By roasting the sulphide until it is partly converted into lead oxide and lead sulphate.

The mixture is now heated without access of air, when the two reactions take place which are represented in these equations:

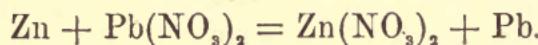


The lead is thus set free, and the sulphur is driven off as sulphur dioxide.

Lead is a bluish-gray metal with a high lustre. It is

very soft and not very strong. It melts at about  $325^{\circ}$ . All lead compounds are poisonous. Nitric acid dissolves it, but hydrochloric and dilute sulphuric acids do not. It is precipitated in metallic form from a solution of one of its salts by metallic zinc. The formation is sometimes called the "lead tree" or "Arbor Saturni."

**EXPERIMENT 174.**—Dissolve 5 grams lead nitrate\* in a litre of water, and put the solution in a bottle. Suspend a piece of granulated zinc in the centre of the solution, and let it stand. The lead will be deposited slowly in crystalline form. At the same time the zinc will pass into solution. The zinc simply replaces the lead:



After the tree has formed, filter off some of the solution and see whether zinc is contained in it or not. There will probably be some lead left, so that in order to detect the zinc the lead will have to be removed first. This may be done by adding sulphuric acid and alcohol. The sulphate of lead is thus formed. As this is somewhat soluble in water and insoluble in alcohol, the latter is added. Filter off the lead sulphate, and to the filtrate add just enough ammonia to neutralize the sulphuric acid, and then ammonium sulphide. White zinc sulphide is precipitated.

If all the lead is not precipitated by the sulphuric acid, the precipitate caused by ammonium sulphide will not be white, but more or less inclined towards black, according to the quantity of lead sulphide present. All the lead may be precipitated in the first instance by first adding some hydrochloric acid [What effect will this have on the solution

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\* Instead of lead nitrate, the acetate or sugar of lead may be used.

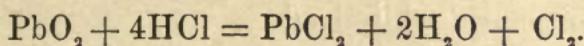
of the lead salt? Which chlorides are insoluble?] and then passing hydrogen sulphide through the solution. Filter off and add ammonia and ammonium sulphide to the filtrate.

Lead forms three distinct compounds with oxygen, viz.: *lead suboxide*,  $Pb_2O$ ; *lead oxide*,  $PbO$ ; and *lead peroxide*,  $PbO_2$ . *Red-lead*, or *minium*, is apparently a mixture of the oxide and peroxide, and has approximately the composition  $Pb_3O_4$ .

*Lead oxide*,  $PbO$ , is known by the name of *litharge*. It is formed by the oxidation of molten lead in contact with the air. When litharge is heated in the air to  $400^\circ$  it takes up oxygen and is converted into the mixture of oxides known as *minium*, or *red-lead*,  $Pb_3O_4 (= 2PbO + PbO_2)$ . When heated to a high temperature it gives up oxygen and is again converted into yellow lead oxide. Treated with nitric acid, a part is dissolved forming lead nitrate, while lead peroxide, a brown powder, remains behind.

**EXPERIMENT 175.**—Treat a little minium with ordinary dilute nitric acid, and note the change in color. [Does lead pass into solution? How do you know?]

*Lead peroxide*,  $PbO_2$ , conducts itself somewhat like manganese dioxide. When treated with hydrochloric acid chlorine is evolved:



**EXPERIMENT 176.**—Treat a little lead peroxide with hydrochloric acid in a test-tube. [In what form is the lead after the experiment? Is the product soluble or insoluble in water?]

Heated with sulphuric acid, oxygen is given off and lead sulphate is formed.

**EXPERIMENT 177.**—Heat some lead oxide with sulphuric acid. Show that oxygen is given off. [What is left behind? Is it soluble or insoluble?]

Among the more important salts of lead are the *sulphate*,  $\text{PbSO}_4$ ; the *nitrate*,  $\text{Pb}(\text{NO}_3)_2$ ; the *carbonate*,  $\text{PbCO}_3$ ; the *acetate*,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ ; the *chromate*,  $\text{PbCO}_4$ ; and the *sulphide*,  $\text{PbS}$ . The acetate and nitrate are soluble in water; the others are not.

**Lead acetate**,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , commonly called “sugar of lead,” is the lead salt of acetic acid,  $\text{C}_2\text{H}_4\text{O}_2$ , which is the acid contained in vinegar. It is formed by dissolving litharge in acetic acid.

The sulphate, chromate, and chloride have already been referred to. They are formed by adding a soluble sulphate, chromate, and chloride to a solution of a lead salt. The chromate is the well-known *chrome yellow*. Lead chloride is soluble in hot water, but only slightly soluble in cold water. It crystallizes from its solution in hot water.

**EXPERIMENT 178.**—To a dilute solution of lead nitrate or acetate add some hydrochloric acid. Heat and thus dissolve the precipitate, and stand it aside. On cooling, the lead chloride will crystallize out. It is not soluble in ammonia. [Does it differ from silver chloride in this respect?]

**Lead carbonate**,  $\text{PbCO}_3$ , is the well-known and much-used pigment called white-lead.

**Lead sulphide**,  $\text{PbS}$ , is the important mineral galenite to which reference has been made. The compound is precipitated by passing hydrogen sulphide through a solution of a lead salt, or by adding a soluble sulphide to such a solution.

[How can you distinguish between a lead and a barium salt without using hydrogen sulphide? Between lead and

silver without using hydrogen sulphide or hydrochloric acid? By hydrochloric acid alone?]

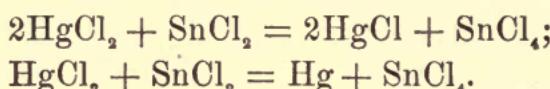
**Tin, Sn (At Wt. 118).**—Tin occurs in nature mostly as tin stone, which is the oxide  $\text{SnO}_2$ . The metal is obtained from the ore by reducing with charcoal. It is a white metal, which in general appearance resembles silver. It is soft and malleable, and can be hammered out into very thin sheets, forming thus the well-known tin-foil. At  $200^\circ$  it is brittle. It melts at  $228^\circ$ . It remains unchanged in the air at ordinary temperatures. It dissolves in hydrochloric acid, forming stannous chloride,  $\text{SnCl}_2$ ; in sulphuric acid, forming stannous sulphate,  $\text{SnSO}_4$ , sulphur dioxide being evolved at the same time [explain this]. Ordinary concentrated nitric acid oxidizes it, the product being a compound of tin, oxygen, and hydrogen, known as *metastannic acid*, which is a white powder insoluble in nitric acid and in water.

Tin forms two classes of compounds, the *stannous* and *stannic* compounds. These do not bear to each other the same relation as that which exists between cuprous and cupric compounds [what is this?], or that between ferrous and ferric compounds [what is this?]. In stannous compounds the tin appears to be bivalent, as indicated by the formulas  $\text{SnCl}_2$ ,  $\text{SnO}$ ,  $\text{SnS}$ , which respectively represent stannous chloride, oxide, and sulphide. In stannic compounds, on the other hand, the tin appears to be quadrivalent, as indicated by the formulas  $\text{SnCl}_4$ ,  $\text{SnO}_2$ ,  $\text{SnS}_2$ , which respectively represent stannic chloride, oxide, and sulphide.

In general, stannous compounds are readily converted into stannic compounds.

**Stannous chloride,  $\text{SnCl}_2$ ,** is formed by dissolving tin in

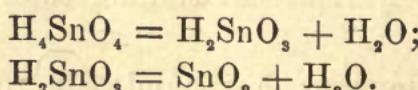
hydrochloric acid. If a solution of stannous chloride be added to a solution of mercuric chloride, or corrosive sublimate, the latter is reduced to mercurous chloride, and this, being insoluble in water, appears as a precipitate. When stannous chloride and mercuric chloride are heated together in solution, metallic mercury is formed:



**EXPERIMENT 179.**—Dissolve a few grams of tin in ordinary dilute hydrochloric acid. Add a little of this solution to a solution of mercuric chloride. A white precipitate of mercurous chloride will be formed. Heat the two solutions together, and notice the formation of metallic mercury, which appears as a gray powder.

**Stannic oxide,**  $\text{SnO}_2$ , occurs in nature as tin stone. It is obtained by burning tin in the air. When melted together with caustic soda it dissolves as sodium stannate. This action suggests that which takes place when silicon dioxide is melted with an alkali and a silicate is formed, and when carbon dioxide and an alkali are brought together. The formulas of the products in these cases are similar, viz.:  $\text{Na}_2\text{SnO}_3$ ,  $\text{Na}_2\text{SiO}_3$ , and  $\text{Na}_2\text{CO}_3$ .

**Metastannic acid,**  $\text{SnO}_4\text{H}_4$ , is formed by oxidizing tin with ordinary concentrated nitric acid. At  $100^\circ$  it is converted into stannic acid,  $\text{H}_2\text{SnO}_3$ , and at red heat into stannic oxide,  $\text{SnO}_2$ :



[Are there any analogous facts known in connection with silicon? Compare the oxides and acids of carbon, silicon,

and tin, not only as regards their formulas, but as regards their properties and transformations.]

**Stannic chloride**,  $\text{SnCl}_4$ , is made by heating tin in chlorine. It is a heavy liquid, which distils at  $120^\circ$  without suffering decomposition. It fumes in the air very strongly. It has a marked affinity for water, and is used as a dehydrating agent in a number of reactions. In solution it is obtained by dissolving tin in aqua regia. In this case the stannous chloride formed by the action of the hydrochloric acid on the tin is oxidized by the nitric acid:



[What happens when a solution containing ferrous chloride is treated with nitric acid?]

**Stannic sulphide**,  $\text{SnS}_2$ , is a yellow substance looking like arsenic sulphide. It is formed by passing hydrogen sulphide through a dilute solution of stannic chloride. It is soluble in yellow ammonium sulphide.

**EXPERIMENT 180.**—Dissolve a little tin in aqua regia. Make the solution very dilute, and pass hydrogen sulphide through it. Filter off, wash, and treat with yellow ammonium sulphide. [Does the precipitate dissolve? Add an acid to the solution. What takes place?]

Tin is used very extensively in the manufacture of utensils of various sorts, and in preparing several valuable alloys. Among these are solder, which consists of tin and lead; britannia, which consists of 9 parts of tin and 1 part of antimony; bronze, which consists of tin and copper.

A peculiarity of tin which distinguishes it from most other metals is its conduct towards nitric acid. As already stated, instead of dissolving in the acid, it is converted into a white, insoluble compound,—metastannic acid. Anti-

mony is also converted into a white oxide by nitric acid, but antimony does not dissolve in hydrochloric acid, while tin does.

**EXPERIMENT 181.**—Treat a little tin with strong nitric acid, and notice the formation of the white metastannic acid. [Is it soluble in water?] Treat a little antimony in the same way. Now treat each element separately with hydrochloric acid.

**EXPERIMENT 182.**—Examine a small piece of solder, and show that it contains lead and tin. Treat with aqua regia; dilute with water. [Will all the lead pass into solution under these circumstances? Will any of it?] Pass hydrogen sulphide through the much-diluted solution. Filter off the precipitate; wash with hot water; treat with yellow ammonium sulphide; filter; add an acid to the filtrate. [Explain what takes place in each step.] The formation of a yellow precipitate, which is soluble in yellow ammonium sulphide, is not conclusive evidence that tin is present, for arsenic sulphide has similar properties. In order to distinguish between them advantage may be taken of the fact that arsenic sulphide is soluble in a solution of ammonium carbonate, while stannic sulphide is not. Treat some of the precipitate with a solution of ammonium carbonate; filter; add an acid, when, if any arsenic sulphide is in solution, it will be precipitated.

**EXPERIMENT 183.**—Examine a small piece of bronze, and show that it consists of tin and copper. In this case, after getting the two metals in solution, by means of aqua regia, dilute and pass hydrogen sulphide through until the solution is saturated. Filter; wash; treat with yellow ammonium sulphide. Filter; acidify; prove that the yellow precipitate is not arsenic sulphide. Dissolve the black pre-

cipitate, which is mostly insoluble in ammonium sulphide, in nitric acid. [What change will the copper sulphide undergo when treated with nitric acid?] Treat a little of the solution with caustic soda, and boil. [What changes take place?] Filter and wash. Mix some of the black precipitate with sodium carbonate, and heat in the reducing flame of the blow-pipe. [What evidence do you then get of the presence of copper?]

Palladium, ruthenium, and rhodium are three rare elements which closely resemble one another.

Palladium forms with hydrogen a compound which in general has the properties of alloys. It has the composition  $\text{Pd}_2\text{H}$ , and contains about 600 volumes of hydrogen to 1 volume of palladium. The properties of this substance have led to the view that hydrogen has metallic properties. If by the name metal is meant an element which forms salts with acids, then it may be said that hydrogen bears to other metals a relation similar to that which carbonic acid bears to other acids. Acids are simply salts of hydrogen, and other metals drive out the hydrogen. Carbonates are in the same way decomposed by all other acids.

Platinum, osmium, iridium, and gold form a family in which, however, the three first mentioned are the most closely related. Of these three, platinum is the best known.

Platinum, Pt (At. Wt. 194.8), occurs almost always accompanied by iridium, palladium, rhodium, ruthenium, and osmium, in the form of alloys. The ore is found in the Ural Mountains, in California, Australia, and a few other places. It is prepared by treating the ore with strong aqua regia, which dissolves the platinum, together with some iridium. The platinum chloride thus obtained

is precipitated by means of ammonium chloride, with which, as with potassium chloride (see p. 319), it forms a difficultly soluble compound,  $\text{PtCl}_4 + 2\text{NH}_4\text{Cl}$ , or  $(\text{NH}_4)_2\text{PtCl}_6$ . When this is heated to a sufficiently high temperature it is decomposed, leaving metallic platinum as a residue. By special methods the iridium can be separated from it.

Platinum is a grayish-white metal, with a high lustre. Its specific gravity is 21.15, it being one of the heaviest substances known. The specific gravity of iron is 7.8, that of lead 11.4, and that of lithium 0.59. In other words, a piece of platinum weighs nearly three times as much as a piece of iron of the same dimensions, and nearly twice as much as a piece of lead of the same dimensions. Platinum is not dissolved by hydrochloric, nitric, or sulphuric acid; but aqua regia dissolves it, forming platinum chloride,  $\text{PtCl}_4$ . Fusing caustic alkalies attack it; sodium carbonate does not. It does not change in the air, and does not melt except in the flame of the oxyhydrogen blowpipe. It resists the action of most substances. These properties make it extremely valuable to the chemist. Platinum crucibles and evaporating-dishes, foil, and wire are constantly used in the laboratory, and it is difficult to see how we could get along without them. Large retorts of platinum are used for the purpose of concentrating sulphuric acid and distilling it.

**Platinum chloride,  $\text{PtCl}_4$ ,** is made by dissolving the metal in aqua regia and evaporating off the acids. It dissolves in water, forming a yellowish-red-colored solution, which is used in the laboratory for the purpose of precipitating potassium from its solutions, as the salt *potassium chloroplatinate*,  $\text{K}_2\text{PtCl}_6$ , or  $\text{PtCl}_4 + 2\text{KCl}$ , is difficultly soluble

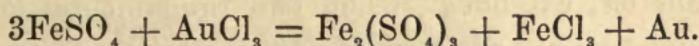
in water. The corresponding sodium salt,  $\text{Na}_2\text{PtCl}_6 + 6\text{H}_2\text{O}$ , is easily soluble in water. There is another chloride of platinum of the formula  $\text{PtCl}_2$ , known as *platinous chloride*.

Platinum chloride combines with ammonia in a great many different proportions, forming the so-called *platinum bases*. The discussion of these compounds would lead us too far at present.

**Gold, Au (At. Wt. 196.7).**—Gold usually occurs native. It is found enclosed in quartz, or more frequently in quartz sand. It is separated mechanically by washing, and then extracted with mercury, which forms an amalgam with it. The amalgam is afterwards heated, when the mercury passes over and the gold remains behind.

Gold is a yellow metal with a high lustre. It is quite soft and extremely malleable. Its specific gravity is 19.3.

It combines directly with chlorine, but not with oxygen. The three acids hydrochloric, nitric, and sulphuric acid do not act upon it; but aqua regia dissolves it, forming gold chloride. From its solutions it is thrown down in uncombined condition by various reducing agents, as, for example, ferrous sulphate,  $\text{FeSO}_4$ :



Goldware and coin are made of an alloy of gold and copper. The standard gold coin of the United States contains nine parts of gold to one of copper. The composition of gold used for jewelry is usually stated in terms of carats. Pure gold is 24-carat gold; 20-carat gold contains 20 parts gold and 4 parts copper; 18-carat gold contains 18 parts gold and 6 parts copper, etc.

## CHAPTER XXVI.

### GENERAL CONSIDERATIONS.—NATURAL GROUPS OF ELEMENTS.—CONCLUSION.

WE have now studied a number of the chemical elements and the way they act upon one another. We have also made the acquaintance of a goodly number of chemical compounds, and have studied to some extent their action upon one another. We have learned that there are certain characteristics which distinguish chemical action from all other kinds of action; and that there are laws governing all cases of chemical action, as there are laws governing the motions of the heavenly bodies. These laws were discovered by careful study of a large number of cases. When it was found that they hold true in the cases studied, it was assumed that they hold true in all cases. The law is only a statement of what is found to be true so far as examination has extended. The two fundamental laws of chemical action are the laws of definite and multiple proportions, but a great many more laws must be discovered before we can form any conception in regard to the real cause of chemical action. The facts which we have become acquainted with thus far show that the chemical elements differ from one another very markedly. Some, like chlorine, phosphorus, potassium, are extremely active; while others, like nitrogen, are inert. Some chemical reactions take place violently, others with scarcely a perceptible evo-

lution of heat. Why these differences? Why does chlorine attack and combine with nearly every other element, while gold can scarcely be made to unite with other elements? Why does chlorine combine with hydrogen, volume for volume, while oxygen combines with the same element in the proportion of one volume to two; and nitrogen in the proportion of one to three, etc.? What are the differences which we recognize under the name of valence due to? Why do some elements resemble one another closely, so that a relationship is recognized at once? Is there any connection between the families of the elements? Why are some substances acids and some bases? What is the real difference between acids and bases? Why can chlorine and nitrogen combine with oxygen in so many different proportions, while potassium, calcium, and other elements combine with oxygen in only one proportion? These are some of the questions which will suggest themselves to the student. But the questions cannot be answered at present. The answers can only be given by long-continued painstaking investigation of the facts of chemistry; or, in other words, by the same means that has made chemistry what it is to-day. The amount of work it has taken to establish the facts considered in this work is enormous. It began away back in the dark ages, and has continued with increasing energy to the present. The science of chemistry is the result of this work. Nothing mysterious has been involved in the growth. There are always those who have the desire to learn more than is known in regard to the matters with which they are occupied. If the desire leads to actual work, undertaken for the purpose of enlarging knowledge, something of value is sure to be learned. Most important discoveries have been

made as the result of investigations in regard to comparatively simple phenomena. One thing suggests another, until, by a consideration of a number of facts, relations are seen which were not dreamed of before, and things which appeared difficult become simple. The time will come when the connection between the facts of chemistry will be discerned. It will then no longer be a difficult thing to classify the elements. They will be seen to form a natural series in which each element has its place, and the properties of the elements will be seen to be determined by the place which they occupy in the system. Indeed, the time has already come when it can be shown that there is a close connection between the atomic weights of the elements and many of their other properties. While it is not possible to discuss this subject with any degree of fulness at present, a brief account will serve to give an idea of the character of the connection.

Attention has repeatedly been called to the curious relations existing between the atomic weights of members of the same family of elements, as in the case of chlorine, bromine, and iodine; calcium, strontium, and barium; lithium, sodium, and potassium, and others. A careful study has shown that these relations are more extensive than appears at first sight. If, leaving out hydrogen, and beginning with lithium, which next to hydrogen has the lowest atomic weight, we arrange the elements in the order of their atomic weights, the first fourteen will exhibit a most remarkable relation, as is shown in the subjoined table:

Li = 7; Cl = 9.1; B = 11; C = 12; N = 14; O = 16; F = 19;  
Na = 23; Mg = 24; Al = 27; Si = 28; P = 31; S = 32; Cl = 35.5.

The elements whose symbols stand under each other in this table have similar chemical properties. This is marked in the case of lithium and sodium ; carbon and silicon ; nitrogen and phosphorus ; oxygen and sulphur ; and fluorine and chlorine. Proceeding in the same way, the element with the next higher atomic weight is potassium, 39.1. This comes in the same perpendicular line with lithium and sodium or with members of the same family. Then follow calcium, scandium, titanium, vanadium, chromium, and manganese, each of which falls naturally in the perpendicular line which contains elements allied to it. It has been found possible in this way to arrange all the elements in one table which exhibits the relations between their atomic weights and properties. Several tables have been proposed, but they do not differ essentially from one another. That suggested by the Russian chemist Mendeleeff is here given. The atomic weights used in the table have been calculated with care from the results of the most trustworthy determinations made by different chemists. In some cases they will be found to differ slightly from those in common use :



It will be seen that in Group I. are the metals of the alkalies; in Group II., calcium, strontium, and barium, magnesium, zinc, and cadmium ; in Group IV., carbon, silicon, tin, lead ; in Group V., nitrogen, phosphorus, vanadium, arsenic, etc.; in Group VI., sulphur, selenium, tellurium, chromium, molybdenum ; in Group VII., fluorine, chlorine, bromine, and iodine, and manganese. Between the fourth series ending with manganese and the next one beginning with copper there are three similar elements, iron, cobalt, and nickel. So, too, a similar group of three elements—ruthenium, rhodium, and palladium—comes between the the sixth and seventh series; and another, consisting of osmium, iridium, and platinum, between the tenth and eleventh. Passing from left to right in each series, we find that the elements can combine with a larger and larger relative quantity of oxygen. The only oxygen compound of lithium has the formula  $\text{Li}_2\text{O}$ . The oxide of glucinum is  $\text{GLO}$ ; that of boron,  $\text{B}_2\text{O}_3$ ; that of carbon, which contains the largest proportion of oxygen, is  $\text{CO}_2$ ; that of nitrogen,  $\text{N}_2\text{O}_5$ ; that of sulphur,  $\text{SO}_3$ ; and that of chlorine,  $\text{Cl}_2\text{O}_7$ . On the other hand, the power to combine with hydrogen increases until a limit is reached as we pass from right to left, as is shown in the compounds  $\text{FH}$ ,  $\text{OH}_2$ ,  $\text{NH}_3$ , and  $\text{CH}_4$ .

Those elements which have the strongest metallic character, whose hydroxides are the strongest bases, are included in Group I. The hydroxides of the metals in Group II. are weaker bases, those of the elements in Group III. are weaker still, while when we reach Group IV. the hydroxides of some of the elements included in it have weak acid properties and no basic properties. The elements of Group V. are nearly all acid-forming. Those of Group

VI. form strong acids, as do those of Group VII. If we know the atomic weight of an element we can say approximately where it belongs in the table, and can from its position determine its properties with considerable accuracy. When the table was first constructed, the two elements scandium and gallium were undiscovered. It was seen, however, that the gaps existed, and it was predicted that elements would be found with atomic weights approximately 44 and 69 respectively, and that these elements would have certain properties which were clearly described. It was suggested that the element with the atomic weight 44 would bear to calcium and titanium about the same relation that aluminium bears to magnesium and silicon. The predictions were soon after confirmed, and the description of the element given before it was discovered was found to be singularly correct. Unquestionably the properties of the elements are determined by their atomic weights. An element whose atom weighs 100 times as much as that of hydrogen must have certain definite properties. It must combine with hydrogen and with oxygen in certain proportions; it must be allied to the members of the chlorine family; its properties are the result of that particular weight. Further, it seems to follow that the elements are not entirely independent forms of matter, but that they are in all probability compounds of a small number of simple elements at present unknown to us. Of this, however, we have no evidence, and until some one succeeds in isolating one or more of these subtler elements it is almost useless to speculate in regard to them.

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## APPARATUS AND CHEMICALS.

WITH two or three exceptions, all the experiments described in this book can be performed in any chemical laboratory. The apparatus needed is of the simplest kind, and the chemicals are such as can be obtained without difficulty. For the benefit of those who have no laboratory at command, and who may wish to make arrangements for going through with the experimental work, the following list has been drawn up. In it is included everything necessary to perform the experiments on a small scale. Should it be desired to fit up a room with conveniences for students, the amount of apparatus necessary would depend upon the number of students, but for each individual the expense would be small, as many of the pieces of apparatus, such as the galvanic battery, burette, weights, scales, etc., need not be multiplied. In place of some of the pieces of apparatus described in the book, ordinary kitchen utensils will answer: thus, for example, instead of the trough for collecting gases, a tin pan or a deep earthenware dish may be used; instead of the water-bath, a stew-pan, fitted with two or three different-sized tin or sheet-iron rings; and in place of glass cylinders for working with gases, wide-mouthed cheap bottles.

The publishers do not deal in chemicals and apparatus, nor, they may as well say, receive commissions on them. Any orders should be sent direct to the dealer. Those whose names are at the end of this list, the publishers take the responsibility of recommending as thoroughly reliable.

## APPARATUS.

12 Test-tubes, 5 in.....	\$0 35	4 oz. Potass. Permangan., bottle.	\$0 30
1 Test-tube Stand.....	30	4 oz. Caust. Soda, purif., bottle..	25
1 Bunsen's Burner.....	50	4 oz. Caust. Ammonia, bottle....	20
1/4 lb. Germ. Glass-tubing.....	15	4 oz. Ammon. Chloride, box.....	10
1 Triang. File, 4 1/2 in.....	25	4 oz. Metall. Lead, box.....	10
1 Round File, 5 in.....	25	4 oz. Ammon. Nitrate, bottle....	20
2 Bunsen's Cells, pt., 1.20.....	2 40	4 oz. White Arsenic, bottle.....	12
2 Wire Clamp Supports, 75 c.....	1 50	4 oz. Fluorspar, powd., box.....	10
1 Porcel. Mortar 3 1/4 in. and pestle	50	2 oz. Potass. Bromide, bottle....	15
1 Horseshoe Magnet, 3 in.....	20	1 oz. Potass. Iodide, bottle.....	35
2 Watch-glasses, 2 in.....	10	1/2 lb. Iron Sulphide, box.....	15
2 Porcel. Dishes, 1 ea. 2 1/2 and 3 1/2 in.....	40	2 oz. Lead Nitrate, box.....	10
1 Iron Tripod.....	25	1 oz. Red Phosphorus, bottle.....	25
1 Mohr's Burette, 25 in 1/10 c.c.....	1 25	4 oz. Caust. Potassa, bottle.....	25
1 Hess. Crucible, 4 oz.....	6	4 oz. Met. Antimony, box.....	10
1 Deflagrat. Spoon.....	20	2 oz. Tartar Emetic, powd., bottle	20
1 Stopper Retort, 2 oz.....	30	4 oz. Borax, box.....	10
6 Florence Flasks, 1-4 oz., 15 c.; 2-6 oz., 18 c.; 2-8 oz., 22 c.; 1-12 oz., 25 c.....	1 20	4 oz. Fine Iron Filings, box.....	10
1 set Cork Borers of brass, 6; set.	1 50	4 oz. Carbon Disulphide, bottle..	15
1 Glass Tube, 12-15 in. l., 1-1 1/4 in. bore, one end closed.....	50	8 oz. Hydrochlor. Acid, bottle...	20
2 Funnel Tubes, assort.....	40	8 oz. Nitric Acid, bottle.....	20
1 set Gramme Weights, 20.0-0.01, in box.....	65	1 lb. Sulphuric Acid, bottle.....	20
1 pr. Hand Scales, E. & A. 3041..	85	8 oz. Copperfoil.....	35
2 doz. Assort. Corks.....	18	1/2 drm. Magnesium Ribbon.....	40
1 Platin. Foil, 1 1/2 in. square.....	50	4 oz. Magnesium Sulphate, box..	10
1 Quire Filter-paper .....	35	2 oz. Barium Chloride, box.....	10
1 Measur. Glass., 25 c.c.....	45	1 oz. Iodine, gl. st. bottle.....	45
6 inch. Platin. Wire.....	15	2 oz. Strontium Nitrate, bottle..	10
1 Jewellers' Blowpipe, 8 in.....	20	4 oz. Potass. Sulphate, box.....	10
3 ft. Gas Rubber Tubing.....	40	1 oz. Litmus, box.....	10
2 ft. Gas Rubber for connect. ass.	25	1 Sheet each Blue and Red Lit- mus paper.....	10

## CHEMICALS.

1/2 lb. Roll Sulphur, in box.....	10	4 oz. Sodium Carbon. Anhydr., purif., box.....	10
4 oz. Granul. Tin, in box.....	15	4 oz. Bleach. Powder, bottle.....	10
4 oz. Potass. Chlorate, in box.....	12	4 oz. Ammon. Carbonate, bottle..	10
1 lb. Mangan. Dioxide, in box....	15	2 oz. Sodium Phosphate Cryst., bottle.....	15
1 oz. Phosphorus, in bottle.....	20	2 oz. Mercury, bottle.....	15
1 drm. Sodium, in bottle.....	15	4 oz. Alum, box.....	10
1 drm. Potassium, in bottle.....	52	4 oz. Potass. Dichromate, box...	10
1 lb. Granul. Zinc.....	25	1 oz. Metall. Bismuth, box.....	25
4 oz. Calcin. Gypsum, box.....	10	4 oz. Minium, box.....	10
4 oz. Sodium Sulphate, in box... ..	10	4 oz. Litharge, box.....	10
4 oz. Calcium Choride, bottle....	15	1 oz. Lead Peroxide, comm. bot.	15
		4 oz. Copper Sulphate, box.....	10
		2 Boxes, and delivered free on board, N. Y. City.....	1 00
			\$26 70

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